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THE DECOMPOSITION OF WATER BY RADIATION

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February 10, 1950.

Berkeley, California
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SUMMARY
THE DECOMPOSITION OF WATER BY RADIATION

In order to account for the observed decomposition of water by radiation (i.e., x-rays, protons, alphas, extreme ultra-violet, etc.), it has been suggested that the primary effect of the irradiation of water is the creation of H-atoms and OH free radicals. This hypothesis has been found to be fruitful and satisfactory within the limits of this dissertation. A general analysis of the problem indicates that the decomposition of water is dependent on (a) the rate of energy loss of the radiation, (b) the rate of diffusion, (c) the interaction of the decomposition products with the H and OH free radicals, (d) the probability of capture while in a solvent cage, and (e) the purity of water.

The decomposition of air-free water by radiation falls, essentially, into two groups. In one group the decomposition of water is large with the result that the number of H₂ and H₂O₂ molecules is almost equal to the number of ion-pairs created by the radiation. This group is characterized by only that type of radiation in which the rate of energy loss is greater than 70 Mev/gm/cm² of water. This corresponds to energies less than 6 Mev for protons and 125 Mev for alphas. The second group includes all radiation with a lower rate of energy loss and is characterized by a total decomposition which is small and difficult to evaluate since minute impurities in the water introduce additional complicating factors.

In order to determine the detailed mechanisms that control the decomposition of water, it became necessary to study the influence of O₂, H₂ and H₂O₂ on the decomposition of water: (a) O₂ has a high affinity for H-atoms and, therefore, its presence prevents a recombination of the H and OH free radicals; (b) the effect of H₂ in an O₂ aqueous solution is to eliminate the interaction of OH and HO₂ and, therefore, enhance the formation of H₂O₂; (c) the effect of H₂ on a H₂O₂ aqueous solution, on the other hand, is to enhance the decomposition of H₂O₂.
Thus from these and other experiments it was possible to determine the influence of H, OH, and HO₂ free radicals in the decomposition of water.

The most distinctive feature for any of the free radical reactions, however, was the probability of capture while in the solvent cage. Once this factor has been determined, then the range and lifetime of the radicals can be calculated for any given set of conditions. The probability of capture while in the solvent cage depends on the type of interaction; radical-radical interactions have a probability which is close to unity while radical-molecule interaction probabilities may be as small as 10⁻⁶ and depend, in the main, on the type of radical rather than the molecule. Among the free radicals, the H-atom is predominantly active, mainly, because of its relatively simple structure and its ability to diffuse rapidly. The OH is next with the HO₂ being the least active of the three.
Part I
Decomposition by Protons, Alphas, and X-rays

I. INTRODUCTION

The purpose of the experiments described herein is to determine in greater detail the mechanism by which water decomposes in the presence of radiation. The experimental evidence, so far, appears to be meager and, in some cases, contradictory. Consequently, the mechanism for the decomposition of water is quite vague and incomplete. In a larger sense, this process is fundamental in any experiments involving matter in which the water content is large. This is particularly true in biological experiments with x-rays and radioactive sources. Thus a concerted effort to further clarify the subject appears to be very desirable.

The decomposition of water by radiation attracted attention early in the century and, initially, in search for clues that might lead to the solution of the mysteries surrounding radioactivity. Considerable work was done with alpha- and beta-rays (Li28).* The primary decomposition products were found to be hydrogen and hydrogen peroxide, while oxygen appeared as a secondary decomposition of hydrogen peroxide. Comparison of the number of water molecules decomposed with the number of ion-pairs created by alpha-rays showed that they were almost equal. In the case of betas, however, the number of water molecules decomposed was found to be considerably smaller.

1.1 Historical Summary. The first informative experiments were recorded by Cameron and Ramsay in 1907-1908 (Li28, p. 76). They used radon dissolved in water as a source of alphas and concluded that the rate of reaction is always proportional to the quantity of radon present. The ionic yield, \( \frac{M}{N} \), determined by

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* Refers to list of references in last part of the report. In addition, the page number will also be included whenever necessary.
this method, has been found to be 0.78 (Nu34) and 0.72 (La38) water molecules decomposed per ion-pair. Another measurement, in which only the H₂O₂ was recorded, shows that 0.17 H₂O₂ molecules are formed per ion-pair (Bo48). This is, essentially, equivalent to the decomposition of 0.34 water molecules per ion-pair.

In order to confine the radon within a small and restricted region, Duane and Schueuer employed in 1913 (Li28, p. 104) a small glass bulb with very thin walls. Thus this geometry was desirable but it had a serious disadvantage in that most of the alpha energy was spent in penetrating the glass walls. Their measurements indicate that M/N = 0.86-1.05. Using the same method, Lanning and Lind (La38) found an M/N = 0.87.

Kernbaum (Li28) reported that H₂O₂ is formed in small quantities when betas from radioactive sources are used to irradiate water. Moreover, he found that the gas evolved during irradiation is pure hydrogen. Some experiments with x-rays indicate similar results while others deny the existence of H₂O₂ in the irradiated water. Fricke's (Fr33, Fr34) analysis of the decomposition products showed that no H₂O₂ was detectable. He attributed the gaseous decomposition products of H₂ and CO₂ to the existence of a small concentration of organic matter in the carefully purified water. Therefore, he concluded, x-rays purify water rather than decompose it. The results of Bonet-Maury (Bo48) were also negative. It should be noted, however, that the volume of the irradiation unit used by Fricke was 20 cc, whereas, that of Bonet-Maury appears to have been no bigger than 3 cc (Bo44). The latter capacity is definitely too small and may, in part, account for the failure to observe any H₂O₂.

On the other hand, A. O. Allen (Al48) claims that purified water decomposes into H₂ and H₂O₂ when exposed to one Mev electrons or x-rays. His results correspond, approximately, to an initial yield of 0.1 H₂ molecules per ion-pair.
Concerning $H_2O_2$, he merely states that it exists in comparable amounts but gives no definite or further information. It appears that if the $H_2O_2$ was comparable to the amount of $H_2$, then it would have been more consistent and easier to titrate for $H_2O_2$ than to measure the pressure of $H_2$.

In addition, Allen observed that the evolution of hydrogen did not increase indefinitely but reached a finite steady state pressure which was a function of both the density and energy of the radiation (Al46). He gives a pressure of 1-2 cm (Hg) for high energy electrons and 10-20 cm (Hg) for tritium betas. The cause of this equilibrium he ascribes to back reactions. The principal of these is the interaction of $H_2$ with the OH free radical.

Of the types of radiation not already mentioned, the most important are the neutron, proton, deuteron and the ultraviolet. No information is available on the first two and only a small amount on the last two. The initial yield for 8-Mev deuterons was found to be 0.19 $H_2$ molecules per ion-pair while the steady state pressure has been estimated to be greater than 60 cm (Hg) (Al48). The effect of ultraviolet light on water has also been studied with results that do not differ materially from those for x-rays (Ti6, Fr36).

1.2 The Mechanism of Decomposition. The mechanism by which irradiated water decomposes is a complex process involving a series of events whose existence can only be surmised. Essentially, the processes to be described are based on the formation of hydrogen (H) atoms and hydroxyl (OH) free radicals. The essence of this was first suggested by J. Weiss (We44) and in a somewhat different form by Lea (Le47, p. 47) and Burton (Bu47). This hypothetical assumption for the existence of these unionized radicals was necessary to account for the long lifetime of the activation of irradiated water.

The water decomposition process may be summarized as follows: ionizing radiation on passing through water loses energy, in part, by causing water
molecules to ionize; that is,
\[
\text{H}_2\text{O} + \text{ionizing radiation} \rightarrow \text{H}_2\text{O}^+ + e^- \quad (I-1)
\]
The ejected electron, with a mean kinetic energy comparable to its bound energy, will thus have an opportunity to get away from the positive ion and eventually become attached to another molecule or positive ion:
\[
\text{H}_2\text{O} + e^- \rightarrow \text{H}_2\text{O}^- \quad (I-2)
\]
\[
\text{H}_{\text{aq}}^+ + e^- \rightarrow \text{H} \quad (I-3)
\]
where the subscript on the positive ion signifies that the hydrogen ion exists in a structure which involves one or more water molecules. The \( \text{H}_2\text{O}^+ \) ion, on the other hand, remains relatively close to the track of the ionizing radiation since its mass is more than \( 10^4 \) times greater than that of the electron. It readily interacts with its neighboring water molecules and, in the process, leads to dissociation:
\[
\text{H}_2\text{O}^+ \rightarrow \text{H}_{\text{aq}}^+ + \text{OH} \quad (I-4)
\]
Similarly, the greater affinity of the OH radical for the electron causes the \( \text{H}_2\text{O}^- \) of reaction (I-2) to dissociate:
\[
\text{H}_2\text{O} + e^- \rightarrow \text{OH}^- + \text{H} \quad (I-5)
\]
Direct evidence for the existence of reaction (I-5) is meager and inconclusive. The information for this and the other reactions are examined and discussed in some detail by Dainton (Da48).

Therefore, the resultant effect of the irradiation of water is to create free radicals close to the track of the ionizing radiation and H-atoms interspersed in a cylinder which is coaxial with the track. It is estimated that the OH and H free radicals are within a radius of 8 and 150 angstroms, respectively, from the track (Da48, Le47). Thus, in part, this accounts for the difference in
decomposition between alphas and radiation with low density ionization but it is not enough in a quantitative formulation of the detailed mechanism of decomposition. Lack of consistent and extensive experimental evidence has, so far, prevented a satisfactory formulation of the problem.

1.3 The Definition of an Ion-pair. The ion-pair is used exclusively in this report to express the dosage or the amount of energy absorbed by a given configuration. It is used not only for its convenience in x-ray irradiations, in particular, but it is felt that there is considerable amount of significance between an ion-pair and the degree of decomposition, at least, for the problem under consideration. It will be assumed that an ion-pair is created whenever the amount of energy absorbed is 32.5 ev for lightly ionizing radiation and 35 ev for heavily ionizing radiation (Gr44).

Although this evaluation of the ion-pair is based on a gaseous state, there is no particular reason why these values should differ radically in the liquid state. The cohesive forces in the liquid correspond to an energy of one electron-volt or less, whereas, the lowest binding energy of an electron in H2O is 12.6 ev. Consequently, the process of energy absorption in the liquid state should not differ, appreciably, from the gaseous state. However, a roentgen will be assumed to create 10 percent more ion-pairs in a gram of water than in a gram of air to account for the larger absorption in the former.

II. DECOMPOSITION WITH PROTONS AND ALPHAS

2.1 Experimental Techniques. The experimental arrangement used in connection with the University of California 60-inch cyclotron is illustrated in Fig. (I-1). The average energy of the beam on the vacuum side of the aluminum foil has been found to be 37.5 Mev for alphas and 9.45 Mev for protons. On penetrating a 1.5 mil aluminum foil, 13 cm of air path, a 3 mil pyrex window, the beam
arrives at the surface of the water in the irradiation unit with an energy of 31 Mev for alphas and 7.4 Mev for protons.

The irradiation unit shown in Fig. (1-1) consists of pyrex glass with a total volume of 45 cc and usually filled to 2/3 its full capacity with distilled water. A partially filled unit is desirable since it is necessary to shake it violently while bombarding with protons and alphas; that is, the range of the alphas and protons in water is approximately 1.0 mm and, therefore, it becomes necessary to prevent the piling up of decomposition products at the thin window and causing undesirable back reactions.

In order to determine the pressure of the gaseous decomposition products, a long column is attached to the irradiation unit which permits absolute determination of pressure. Initially, all the air is removed from the unit with the aid of a mechanical pump so that only water vapor exists in it. Under these conditions, the water level is the same in both the column and the main part of the vessel. On irradiating the unit with protons or alphas, the water level in the column rises in proportion to the gaseous pressure in terms of centimeters of water. When the column becomes filled and higher pressures are to be measured, the water is allowed to flow out of the column and, at the same time, trapping a certain fraction of the gaseous products in the long column. The pressure in the column is thus calculable with the pressure already recorded and the geometrical dimensions of the unit. Therefore, with this arrangement, low and high pressures may be recorded without the aid of external devices.

A platinum wire is shown attached to the irradiation unit in order to discharge the protons or alphas that are absorbed by the water and also to serve as a means of recording the number of protons or alphas with the aid of an Esterline Angus recorder. A current amplifier was necessary for the latter since the effective beam current was low: 1/3 and 1/10 microamperes for protons and
IRRADIATION UNITS
TOTAL VOLUME = 45 cc.
WATER CONTENT = 2/3 FULL
MATERIAL: PYREX GLASS

FIG. I-1
alphas, respectively. In order to control the duration of the bombardment, accurately, a string operated shutter was found to be very convenient.

The concentration of hydrogen peroxide in the bombarded water was determined by means of the potassium permanganate method. This method allowed a maximum sensitivity of $6 \times 10^{14}$ molecules of $H_2O_2$ per gram of water. Tests for the concentration of oxygen in the gaseous state were carried out with the aid of pyrogallic acid in a basic solution.

2.2 Decomposition with Protons. The decomposition of water by high energy protons represents the missing link which ties in the results of previous experimentalists. At low energies, the decomposition of water, in terms of $H_2O_2$ formation, is large and comparable to that from alphas. At high energies no $H_2O_2$ is detectable and, therefore, the results are comparable to x-rays and electrons. This is experimentally demonstrated in Fig. (I-2) where the number of $H_2O_2$'s produced per proton is plotted against the energy of the protons. The production of $H_2O_2$ per proton rises rapidly for energies up to 3 Mev and then levels off at about 6 Mev. Therefore, raising the energy of the protons above 6 Mev does not contribute to an increase in the concentration of the $H_2O_2$. In fact, the tendency is to decrease the concentration since the radicals created in the higher energy portions of the track are free to attack the $H_2O_2$ already formed in the bombarded water.

The low energy portion of the curve of Fig. (I-2) is drawn in dashed form to indicate the experimental evidence for its shape is indirect; that is, it was drawn so that the slope at zero dosage is high, or $M/N$ approaches unity, since low energy protons are expected to behave like alphas from natural radioactive sources. Moreover, the curve is drawn above the 1.5 Mev experimental point since the latter is subject to a considerable amount of uncertainty arising from the very short, or 0.1 mm, range of these protons in water. This leads to an
accumulation of $H_2O_2$ molecules in a thin film next to the window and, therefore, subject to decomposition by newly created radicals.

Fig. (I-4) illustrates how the gaseous decomposition products rise as a function of the dosage of 7.4 Mev protons. The curve consists, essentially, of two linear portions. The first corresponds to a rate of 0.15 gaseous molecules per ion-pair while the second has a rate of 0.18. Tests for oxygen proved to be negative at lower dosages and positive at higher dosages. Consequently, the implication is that while pure hydrogen is given off during the initial period, oxygen is not evolved until the $H_2O_2$ concentration is high enough to interact with the H and OH free radicals and, therefore, cause its decomposition.

Actually, the pattern presented by Fig. (I-4) is sharply contradicted by the plotted results in Fig. (I-3). The latter predicts that the decomposition of $H_2O_2$, and therefore the formation of $O_2$, begins at dosages which are much smaller than the bend of the curve in Fig. (I-4) would predict. According to Fig. (I-3), the rate of $O_2$ evolution should reach half its maximum value at a dosage of $3 \times 10^{19}$ ion-pairs. In contrast, the same point in Fig. (I-4) appears to occur at a dosage of $13 \times 10^{19}$ ion-pairs. This contradiction hinges on the absorption of oxygen by impurities in the distilled water and will be analyzed further in connection with the irradiation of water by x-rays in the next chapter.

According to Fig. (I-4), the evolution of hydrogen and oxygen rises linearly with the dosage. Actually, the rate of yield for a total dosage of $180 \times 10^{19}$ ion-pairs and a final pressure of 45 cm (Hg) corresponds to 0.07 gaseous molecules per ion-pair. Another sample in which the initial pressure of electrolytic hydrogen and oxygen was one atmosphere gave an average yield of 0.047 gaseous molecules per ion-pair. Thus the gaseous steady state is approached very slowly and will occur at a pressure which is much greater than one atmosphere. It should be noted, however, that the dosage to cause a $H_2O_2$ steady state is much
ENERGY OF PROTONS IN MEV

NO. OF $\text{H}_2\text{O}_2$'S / PROTON

$1 \times 10^4$

$2 \times 10^4$

0 2 4 6 8

ENERGY OF PROTONS IN MEV

FIG. I-2
FIG. I-3
FIG. I-4
smaller than the dosage at which the gaseous yield levels off. Therefore, the mechanism of decomposition for the two cases is not likely to be the same.

2.3 Decomposition by Alphas. A prolonged breakdown in the operation of the 60-inch cyclotron has prevented a detailed study of the alpha-ray properties. However, some measurements were made which bring out the more important characteristics of the decomposition of water by alphas.

On plotting the gaseous decomposition products as a function of the dosage of 31 Mev alphas a curve similar to Fig. (I-4) was obtained. The two linear portions of the curve were more distinct and were characterized by slopes of 0.25 and 0.34 molecules per ion-pair. Hence, the gas evolved, initially, is hydrogen with an ionic yield \( M/N = 2 \times 0.25 = 0.50 \). Later, the yield increases almost 50 percent to account for the decomposition of \( \text{H}_2\text{O}_2 \) and, therefore, the evolution of \( \text{O}_2 \). Thus since the gases evolved are nearly in electrolytic proportion, then in contrast to the case of protons, only a small amount of oxygen appears to be absorbed in reactions with impurities.

In order to account for this difference, it is necessary to compare the relative density of ion-pairs for 7.4 Mev protons and 31 Mev for alphas. A study of the rate of energy loss in water (see next section) shows that the ion-pair density, and therefore the free radical concentration as well, is considerably higher for the alphas. As a result, the number of radicals that are able to escape uncombined from an alpha-track and initiate oxygen absorbing reactions with low concentration impurities is relatively small.

In contrast with Fig. (I-4) but more nearly in agreement with Fig. (I-3), the dosage at which \( \text{O}_2 \) becomes prominent for 31 Mev alphas is \( 10^{19} \) ion-pairs. Analysis of the bombarded water for \( \text{H}_2\text{O}_2 \) showed that the expected steady state concentration is not likely to be much larger than that shown in Fig. (I-3). Of course, the concentration of \( \text{H}_2\text{O}_2 \) is expected to be higher for lower energy alphas since the
probability of radicals escaping uncombined from the track is smaller. This was experimentally verified by Bonet-Maury (Bo48) when he showed that the \( \text{H}_2\text{O}_2 \) formation with radon alphas is a linear function of the dosage, for dosages up to \( 10^{19} \) ion-pairs per gram of water.

### 2.4 Some Analytical Deductions

The experimental results with protons and alphas indicate that the degree of decomposition depends on the density of the free radicals along the track and, therefore, on the rate of energy loss irrespective of the type of radiation. According to Fig. (I-2), the energy at which protons cease to create \( \text{H}_2\text{O}_2 \) is 5 Mev. The rate of energy loss, \(-dE/dx\), at this energy may be determined from (Li37, p. 263)

\[
-\frac{dE}{dx} = \frac{4\pi N z^2 e^4}{mv^2} Z \ln(2mv^2/E) \tag{I-6}
\]

where \( v \) is the velocity of the bombarding particle and \( z \) its charge; \( N \) is the number of atoms per gram of absorbing matter, \( Z \) is the number of electrons per atom, \( m \) is the mass of an electron and \( \overline{E} \) is the average excitation potential for the electrons in the atom.

In order to determine the excitation potential for a water molecule, it will be necessary to consider it as an atom of \( Z = 10 \) electrons but with an average excitation potential defined by the following equation (Li37, p. 271):

\[
(Z \ln 2mv^2/\overline{E})_{\text{H}_2\text{O}} = 2(Z \ln 2mv^2/\overline{E})_{\text{H}} + (Z \ln 2mv^2/\overline{E})_{\text{O}} \tag{I-7}
\]

that is, the effective stopping power of the water molecule considered as an atom is equivalent to the sum of the stopping powers of the atoms of which it is composed. On solving the equation for the average excitation potential for the water molecule, it is found to be

\[
\overline{E}_{\text{H}_2\text{O}} = \overline{E}_{\text{H}}^{1/5} \overline{E}_{\text{O}}^{4/5} \tag{I-8}
\]

The potentials for hydrogen and oxygen are not unique but vary somewhat with the energy of the bombarding particle (Gr 44). For simplicity, however, the
empirical expression $E = 11.5Z$ will be assumed to apply (Wi41). Under these conditions $E_{H_2O} = 62$ ev. Consequently, the rate of energy loss in water may be expressed as

$$-\frac{dE}{dx} = \frac{30z^2A}{E} \ln\left(\frac{33E}{A}\right) \text{ Mev/gm/cm}^2$$

(I-9)

where A is the atomic weight of the corpuscular radiation and E its energy in Mev.

For 6 Mev protons ($-dE/dx = 70$ Mev/gm/cm$^2$), that is, this value represents the critical condition which determines whether any $H_2O_2$ will be observed in the irradiated water or not. In the case of alphas, this same condition should be satisfied at an energy $E = 125$ Mev. The rate of energy loss for low energy electrons is difficult to express accurately but it appears that this condition occurs at an energy of the order of one Kev. Thus to a good approximation electrons and x-rays may be considered as creating a uniform distribution of free radicals throughout the irradiated volume. In the case of highly ionizing protons and alphas, a columnar distribution of radicals may be considered (Ja13) but the calculations are considerably handicapped by the presence of delta-rays (Br48).

III. DECOMPOSITION WITH X-RAYS

The decomposition of distilled air-free water was conducted with x-rays from a source with an accelerating potential of 200 kilovolts peak. The irradiation unit consisted of a disk-shaped vessel made out of pyrex glass. For pressure measuring purposes, a long column was attached to it as in Fig. (I-1). The total volume of the unit was 70 cc. The inside thickness of the unit was only 1/2 inch so that to a good approximation the x-ray energy absorption was uniform throughout the sample of water (Ba23, p. 152). The average rate of dosage of $10.4 \times 10^{16}$ ion-pairs/hr/gm of water was determined by considering not only the field distribution but also the wall thickness of the irradiation unit.
3.1 Experimental Observations. A considerable amount of research was carried out to determine why previous experimentalists observed only pure hydrogen gas from x-ray irradiations of water and why the H$_2$O$_2$ yield was not observed in all cases. As a result a series of experiments were performed with both Barnstead still water and conductivity water. These and other related experiments are enumerated in the following subsections.

a. Barnstead Still Water. Initial attempts to determine the rate of decomposition were based on the assumption that the hydrogen gas being given off during the irradiation was due to impurities in the water. Therefore, according to Fricke (Fr36), an extensive irradiation of the water with x-rays should improve its purity and, as a result, reduce the hydrogen yield to the level where it corresponds to the decomposition of pure water. Initially, the rate of gaseous evolution was 0.09 molecules/ion-pair and decreased to a minimum of 0.03 molecules/ion-pair at a dosage of 200 x 10$^{16}$ ion-pairs/gm of water. At higher dosages, the rate increased rather than decreased or remained constant so that the condition constituting pure water remained unresolved.

A test for H$_2$O$_2$ in an irradiated sample proved to be positive. Further experiments showed that the H$_2$O$_2$ yield rose gradually to a steady state concentration of 4 x 10$^{15}$ molecules/gm of water in a period of ten hours of continuous irradiation. Surprisingly, however, a steady state of 3 x 10$^{15}$ H$_2$O$_2$'s/gm of water was discovered at very low dosages. It was necessary to decrease the exposure to as low a dosage as 5 x 10$^{11}$ ion/pairs/gm of water to decrease the concentration by a factor of two. This is equivalent to a rate of 3000 H$_2$O$_2$'s/ion-pair and must be due to some regenerative reaction.

b. Conductivity Water. X-ray irradiations of air-free conductivity water gave a somewhat different but simpler pattern than the Barnstead still water irradiations. The conclusions, however, are essentially the same. The irradiated conductivity water samples were characterized by initial rates of 0.13 gaseous
molecules/ion-pair which were independent of the amount of irradiation. The \( H_2O_2 \) concentration was very close to the limit of detection with a constant value of \( 10^{15} \) \( H_2O_2 \)'s/gm of water. Thus increasing the purity of the water has a tendency to decrease the \( H_2O_2 \) concentration.

c. Other Observations. The absence of \( O_2 \) in the x-ray decomposition of air-free water suggested the introduction of a small amount of \( O_2 \) in the unit before irradiation. After exposure, an analysis of the gases showed that most of the \( O_2 \) had disappeared and could not be accounted. This immediately suggests that oxygen, in the presence of radiation, is absorbed by some impurity in the water.

Further experiments showed that the highly regenerative process for the formation of \( H_2O_2 \) at extremely low dosages is inhibited in the presence of oxygen. At a total dosage of \( 10^{14} \) ion-pairs/gm of water, the \( H_2O_2 \) yield was reduced by a factor of two in the presence of \( 10^{15} \) \( O_2 \)'s/gm of Barnstead still water. With conductivity water, the effect of \( O_2 \) was not as noticeable since the rubber tubing used in sealing the irradiation unit appears to have been the main source of impurities rather than the water itself. This has a tendency to keep the \( H_2O_2 \) concentration at \( 10^{15} \) molecules/gm of water for concentrations less than \( 10^{16} \) \( O_2 \)'s/gm of water.

The possibility of foreign matter acting as a catalytic agent in the conversion of \( H_2O \) into \( H_2O_2 \) molecules in the presence of radiation is unlikely since such a reaction requires that

\[
2H_2O \rightarrow H_2O_2 + H_2
\]

(1-10)

that is, the hydrogen to be expected from such a reaction should be readily detectable. Tests for \( H_2 \) at low dosages, however, have proved to be negative.

3.2 Analysis of Observations. The experimental observations made in the previous section indicate, quite definitely, the leading role played by impurities in.
the water. An analysis of the concentration of these impurities in the water showed that (Fa39, p. 56-7) the amount of fixed solids in water after a single distillation of tap water was 3.0 milligrams per liter compared to 4.0 milligrams per liter when this water was redistilled by the conductivity water method. Thus pure water is difficult to attain and explains why impurities may be responsible for the absorption of O₂ even though extremely pure water is used (Fr36).

The evolution of pure hydrogen from the irradiation of water does not arise from a direct union of H-atoms

\[ H + H \rightarrow H₂ \] (I-11)

but rather from

\[ H + H₂O₂ \rightarrow HO₂ + H₂ \] (I-12)

The latter reaction is discussed more thoroughly in Part II where it is shown that in an aqueous solution of H₂O₂, the reaction occurs once for every third ion-pair. In order to account for the smaller rate of H₂ yield in air-free water, it becomes necessary to assume that the H-atom rather than the OH reacts with the impurities. This is verified, in part, by the observation that the regenerative process is inhibited by O₂ which has a strong affinity for the H-atom.

Some of the concepts underlying the decomposition of absolutely pure water can be derived from the kinetics of the free radicals. This analysis applies only during the initial period of irradiation when the back reactions with H₂O₂ are not prominent while the H and OH concentrations have reached a steady state. Under those conditions, the probability of chemical interaction of the radicals to form H₂, H₂O₂ and HOH will depend on the relative concentration of H and OH free radicals. Moreover, since the number of H₂ and H₂O₂ molecules must be equal, then the relative free radical concentration can be determined from the Rate Law (Ch43, p. 61) which can be expressed in terms of the formulation in Section 3.1 of Part II:
where the $N$'s represent the concentrations in radicals/gm of water and the $\tau$'s are the average lifetimes of the radicals. The factor of 1/2 on each side of the equation is used to account for the fact that two radicals disappear at each chemical interaction. On using Eq. (II-5), the relative free radical concentration may be expressed as follows:

\[
\frac{N_{OH}^2}{\tau_{OH+OH}} = \frac{N_H^2}{\tau_{H+H}} \tag{I-13a}
\]

\[
\frac{N_{OH}^2}{N_H^2} = \frac{D_{H,H}}{D_{OH,OH}} \frac{\xi_{H,H}}{\xi_{OH,OH}} = 5 \frac{\xi_{H,H}}{\xi_{OH,OH}} \tag{I-13b}
\]

where the diffusion coefficients $D_H$ and $D_{OH}$ are assumed to be $10 \times 10^{-5}$ and $2 \times 10^{-5}$ cm$^2$/sec, respectively. The values of the probability constants $\xi_{H,H}$ and $\xi_{OH,OH}$ are not known but an attempt will be made to estimate them.

In considering the interaction of two radicals in the same solvent cage, the probability of capture is considerably enhanced not only by the finite time of association in the cage but also by the numerous collisions with water molecules to remove the excess reaction energy. In the case of two H-atoms, such a capture is practically certain since they have a very simple structure and no potential barrier to hinder the process. The same argument, essentially, applies for an H-atom to combine with an OH although the structure of the OH is somewhat more complex. In the case of two OH's, however, a potential barrier may exist since the OH's are characterized with electric dipole moments. In considering the maximum dipole force in conjunction with the attractive exchange force in terms of the Morse potential function, the potential barrier for two OH's corresponds to an energy which is less than 4 times the thermal energy at room temperature. This is not a particularly large value and capture may occur in one solvent cage. Thus $\xi_{H,H} = \xi_{H,OH} = 1$ but $\xi_{OH,OH} \ll 1$. Hence, $N_{OH}/N_H \geq 2.2$ and, consequently,
the initial decomposition of water into H₂ and H₂O₂ is certainly not small.

In order to account for the small H₂O₂ yield that is observed with x-rays, it is necessary to consider the back reactions of H₂O₂ with H-atoms. The condition for a steady state will occur when the number of H₂O₂'s destroyed equals those formed. This condition will be satisfied when

\[ \frac{N_{OH}/2}{\tau_{OH+OH}} = \frac{N_{H}}{2 \tau_{H+H_2O_2}} \]  

(I-14)

where the factor of 1/2 on the right side of the equation is used to account for the fact that it requires two H-atoms to destroy one H₂O₂. After substituting for the \( \tau \)'s, the equation may be solved for the H₂O₂ steady state concentration:

\[ N_{H_2O_2} = \frac{D_{OH,OH}}{D_{H,H_2O_2}} \frac{\xi_{OH,OH}}{\xi_{H,H_2O_2}} \frac{N_{OH}}{N_{H}} \frac{N_{OH}}{2} \]  

(I-15)

A numerical value can be calculated, approximately, with the aid of Eqs. (II-3), (II-18), (II-22) and (I-13b)

\[ N_{H_2O_2} \lesssim 0.69 \sqrt{n} \times 10^5 \]  

(I-16)

where \( D_{H_2O_2} \) is assumed to be equal to \( 2 \times 10^{-5} \text{cm}^2/\text{sec} \). Thus the H₂O₂ steady state concentration should be expected to vary as the square root of the rate of dosage n. Since \( n = 29 \times 10^{19} \text{ion-pairs/sec./gm of water} \), then \( N_{H_2O_2} \lesssim 4 \times 10^{14} \text{molecules/gm of water} \) in fair agreement with the concentration observed with conductivity water.

After H₂O₂ equilibrium has been established, the rate of H₂ yield should be of the order of 0.1 molecule/ion-pair since reaction (II-20) occurs half as often as (II-19) while only 1/3 of the H-atoms may be expected to attack the H₂O₂ molecules. The remainder are absorbed in OH and O₂ reactions.

The condition for a gaseous steady state will arise when the number of H₂ molecules produced by reaction (II-20) equals those absorbed by reaction (II-24).
This is satisfied by

\[
\frac{N_H}{\tau_{H + H_2O_2}} = \frac{3}{1} \frac{N_{OH}}{\tau_{OH + H_2}} \tag{I-17}
\]

where the factor of 3/1 is used to account for the relative infrequency of reaction (II-20). Using Eq. (I-15) for \(N_{H_2O_2}\), the steady state concentration for \(H_2\) can be determined from (I-17) after substituting for the \(\tau\)'s.

\[
N_{H_2} = \frac{D_{OH,OH}}{D_{OH,H_2}} \frac{\xi_{OH,OH}}{\xi_{OH,H_2}} \frac{N_{OH}}{N_H} \frac{N_{OH}}{6} \tag{I-18}
\]

On using Eq. (II-26) for \(\xi_{OH,H_2}\) with \(K = 1/2\), Eq. (II-8) for \(N_{OH}\), and \(D_{H_2} = 5 \times 10^{-5} \text{ cm}^2/\text{sec.}\), then

\[
N_{H_2} \sim 4 \times 10^9 \sqrt{n} \tag{I-19}
\]

For \(n = 29 \times 10^{12} \text{ ion-pairs/sec./gm of water, } N_{H_2} = 2 \times 10^{16} \text{ molecules/gm of water. This corresponds to a gaseous pressure of 3 cm (Hg) and is larger only by a factor of two from experimentally observed values. Thus the assumptions used in this derivation must have been approximately correct. Moreover, Eq. (I-19) corroborates A. O. Allen's observation that the steady state pressure varies as the square root of the rate of dosage (A146).}

Thus the agreement between theory and experiment is fair with the exception of very low dosages where impurities appear to determine the initial amount of decomposition. At higher dosages the effect of impurities, for conductivity or pure water, is small but large enough to account for the absorption of the \(O_2\) yield.

IV. CONCLUSIONS

The decomposition of water by protons is typical of the effect of radiation in general. For low energy protons, where the rate of energy loss is high, the
initial yield of $H_2$ and $H_2O_2$ is high. At higher energies where $(-dE/dx) < 70 \text{ Mev/gm/cm}^2$, the decomposition appears to be small and influenced to a considerable degree by minute concentrations of impurities which are also responsible for the absence of oxygen in the gaseous yield. Thus x-rays, $\gamma$-rays, electrons and the extreme ultraviolet can be classified into the latter category. Protons, deuterons and alphas can also be included if their energies are greater than 6, 12 and 125 Mev, respectively. The effect of neutrons will depend on the energy of the recoil protons arising from collisions with the hydrogen atoms in water molecules.

According to the experimental evidence in both Parts I and II, the general pattern of decomposition for air-free water may be summarized as follows: initially, the free radicals created about the track exist, essentially, within two cylindrical regions coaxial with the track of the ionizing radiation; the smaller cylinder with a radius of about 8 angstroms contains the majority of the OH· free radicals; the second cylinder, with a radius which is probably larger than 150 angstroms, contains the majority of the H-atoms; the distribution of the remaining H and OH free radicals depends, in a similar manner, on the tracks of the delta-rays. Thus to a first approximation, the free radicals are segregated from each other and, therefore, favor the formation of $H_2$ and $H_2O_2$ rather than HOH. This is particularly true when the spacing of the OH's along the track is small compared to the radius of the H-atom cylinder. For $(-dE/dx) < 70 \text{ Mev/gm/cm}^2$ of water, these distances are comparable so that a distinct segregation of the radicals no longer exists so that radical recombination into HOH becomes more favorable.

In irradiating air-free water, a steady state concentration for $H_2O_2$ is observed to occur at a dosage that is considerably smaller than the dosage for the gaseous steady state. The mechanism of decomposition for the two cases is quite distinct. The $H_2O_2$ steady state is caused by the interaction of the H-atoms with $H_2O_2$ (refer to Sec. 3.3 Part II). Consequently a steady state will occur when the $H_2O_2$ concentration
is high enough so that the average lifetime $\tau_{H+H_2O_2}$ is smaller than the lifetime of the H-atoms, $\tau_{H+H}$, along the track of an ionizing particle. Since $\tau_{H+H}$ depends on the H-atom concentration and since the latter is proportional to the rate of energy loss, then the steady state concentration for $H_2O_2$ will also be a function of the rate of energy loss and, therefore, the energy of the radiation. Thus the $H_2O_2$ steady state concentration is barely detectable for x-rays and more than 1000 times greater for alphas from radon. As a result, this provides a means of determining the H-atom distribution about the track. However, in order to avoid lengthy bombardments, the use of dissolved $O_2$ in the water should be found to be a preferable means of absorbing H-atoms.

The gaseous steady state is caused, basically, by the interaction of the OH with molecular hydrogen (refer to Section 3.5 in Part II). Here again, the steady state will depend on the rate of energy loss. This is exemplified by a pressure of a few centimeters (Hg) for x-rays to more than one atmosphere for low energy protons and alphas. Thus by introducing various concentrations of $H_2$ into the bombarded water, it should be possible to obtain some information on the OH distribution about the track.
Part II  
Decomposition in Aqueous Solutions of $\text{O}_2$, $\text{H}_2$, and $\text{H}_2\text{O}_2$  

I. INTRODUCTION

The experiments with air-free water in Part I have been informative in a qualitative sense but of little value in establishing a detailed mechanism of decomposition for water when exposed to radiation. To this end, a series of experiments have been performed to determine the actual factors that control the amount of decomposition for a given set of conditions. Aqueous solutions of $\text{O}_2$, $\text{H}_2$ and $\text{H}_2\text{O}_2$ have been irradiated with x-rays from a source operating at 200 kilovolts peak. X-rays rather than protons or alphas were used since the free radicals created by the former may be considered to be distributed uniformly throughout the liquid and, consequently, lead to calculations that are considerably simplified.

Very early in the century, it was observed that the presence of $\text{O}_2$ in water materially contributes to the formation of $\text{H}_2\text{O}_2$. Quantitative experiments, however, have not been sufficiently extensive or broad enough to establish the fundamental processes. Specifically, important information has been missing due to the absence of any experiments with aqueous solutions of $\text{H}_2$ and $\text{H}_2\text{O}_2$.

Fricke’s (Fr34) experiments with $\text{O}_2$ dissolved in water indicate that $\text{H}_2\text{O}_2$ is produced, initially, at a rate of 0.73 molecules per ion-pair. (This assumes that the number of ion-pairs per roentgen is 10 percent greater in a gram of water than in a gram of air since the absorption in the former is greater by 10 percent, approximately.) The extensive measurements of Bonet-Maury (Bo48), however, indicate an initial yield of 0.57 $\text{H}_2\text{O}_2$ molecules per ion-pair at a temperature of 20°C. This yield becomes progressively smaller so that it becomes zero at temperatures below -116°C.
II. EXPERIMENTAL RESULTS

The experimental evidence presented herewith is illustrated in Figs. (II-1) to (II-6). These measurements were made possible with methods and devices already described in Part I and may be summarized as follows: the disk-shaped irradiation unit had a total volume of 70 cc, conductivity water was used in all experiments, the KMnO₄ method was used to titrate for H₂O₂ with a maximum sensitivity of \( 6 \times 10^{14} \) molecules per gram of water, a roentgen is defined as \( 1.77 \times 10^{12} \) ion-pairs per gram of water while an ion-pair appears to be created for each 32.5 ev of energy that is absorbed by the water.

Curves I, II and III of Figs. (II-1) and (II-2) represent the H₂O₂ yield as a function of the dosage and concentration of O₂ in the water. These curves are characterized by two distinct features, first, the initial H₂O₂ yield of 0.80 molecules per ion-pair is independent of the concentration of O₂ in the water and, secondly, the steady state concentration of H₂O₂ in the water corresponds, approximately, to the concentration of O₂. Attempts to replenish any O₂ that might have been absorbed in the process of reaching the steady state failed to increase the H₂O₂ yield after subjecting it to a second irradiation. Moreover, cutting the rate of dosage by as much as a factor of 30 or pulsing the x-ray source had no appreciable effect on the H₂O₂ yield.

However, theory does require that one O₂ molecule should be absorbed whenever two H₂O₂'s are formed. An experimental investigation of the amount of O₂ absorbed showed it to be of the order of 5 to 10 percent for dosages up to \( 10 \times 10^{16} \) ion-pairs/gm of water for Curve III of Fig. (II-1). This does not contradict the theory since back reactions tend to replenish the O₂ in the water; that is, one O₂ molecule is produced whenever two H₂O₂ molecules are destroyed.

Curve IV in Figs. (II-1) and (II-2) corresponds to a mixture of H₂ and O₂ dissolved in water. Thus the presence of H₂ enhances the rate of H₂O₂ formation so that 1.20 molecules per ion-pair are created during the initial period. In
contrast, at higher dosages the \( \text{H}_2\text{O}_2 \) yield reaches a maximum concentration and then declines with dosage. The experimental points of Curve IV were taken with the irradiation unit almost completely filled with water so that the \( \text{O}_2 \) from the gaseous phase could not diffuse readily into the liquid. When a partially filled unit was used instead and shaken periodically, the \( \text{H}_2\text{O}_2 \) yield is similar in form to Curve III but with a steady state concentration of \( 1.7 \times 10^{16} \text{H}_2\text{O}_2\text{s/gm} \) of water—practically the same concentration as the oxygen content of the water. Thus in the presence of \( \text{H}_2 \), oxygen is continuously absorbed, the end result of which is the formation of water or \( 2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O} \), for large dosages.

Increasing the \( \text{H}_2 \) concentration by as much as a factor of 5 had no discernable effect on the \( \text{H}_2\text{O}_2 \) yield indicated on Curve IV at low dosages. On the other hand, on decreasing the concentration of \( \text{H}_2 \) to \( 3.2 \times 10^{16} \text{molecules/gm} \) of water, the initial yield dropped to 0.95 \( \text{H}_2\text{O}_2\text{s/ion-pair} \). This is illustrated by Curve V in Fig. (II-2). Experiments in which only \( \text{H}_2 \) was dissolved in water showed that the \( \text{H}_2\text{O}_2 \) yield did not differ, materially, from that observed with air-free conductivity water.

Fig. (II-3) illustrates the behavior of aqueous solutions of \( \text{H}_2\text{O}_2 \) when exposed to x-rays. The initial rates of \( \text{H}_2\text{O}_2 \) decomposition are 0.43, 0.63 and 0.80 molecules/ion-pair for Curves I, II, and III, respectively. The tendency for these curves is to approach zero rather than a steady state as in Fig. (II-2) since most of the \( \text{O}_2 \) was able to escape into the gaseous space above the liquid or absorbed, in part, in reactions with impurities. The gaseous yield curve in Fig. (II-3) had an initial and final concentration of \( 16.5 \times 10^{16} \text{and} 2.9 \times 10^{16} \text{H}_2\text{O}_2\text{s/gm} \) of water, respectively. The initial yield for this curve corresponds to 0.58 gaseous molecules/ion-pair. Using the pyrogallic acid method, the oxygen content for this sample was found to be 45 percent. A second and similar sample showed that at the lower dosage of \( 7.8 \times 10^{16} \text{ion-pairs/gm} \) of water the relative
Fig. II-1
\[
N_{O_2} = 16.3 \times 10^{16} \\
N_{H_2} = 19.0 \times 10^{16}
\]

\[
N_{O_2} = 16.3 \times 10^{16} \\
N_{H_2} = 3.2 \times 10^{16}
\]

\[
N_{O_2} = 16.3 \times 10^{16} \\
N_{O_2} = 1.63 \times 10^{16}
\]

\[
N_{O_2} = 0.16 \times 10^{16}
\]

FIG. II-2
FIG.II-3
amount of O\textsubscript{2} was still the same. Thus, approximately, \(\frac{1}{3} \text{H}_2\)'s/ion-pair may be expected to be produced, initially.

Figs. (II-4) and (II-5) illustrate the effect of introducing H\textsubscript{2} into a solution of H\textsubscript{2}O\textsubscript{2}. The resultant effect is to enhance, greatly, the process of the decomposition of H\textsubscript{2}O\textsubscript{2}. The initial rate of decomposition in Fig. (II-4) jumps from 0.68 in a solution without any hydrogen to 3.0 molecules/ion-pair in the presence of hydrogen. In fact, the dashed portion of the curve indicates that a higher and critical rate of decomposition exists in that region. A similar but more extreme situation is shown in Fig. (II-5); that is, although equal care was taken for all experimental points, yet, there exists a wide divergence in the uniformity of the two curves. Only a critical chain reaction can, probably, account for such a wide diversity in these observations.

The curves of Fig. (II-6) were determined for the purpose of establishing the influence of temperature on irradiated aqueous solutions. The total dosage was chosen low in order to avoid a multiplicity of reactions. The results, however, are anything but simple since the temperature coefficient is negative at room temperature and fluctuates rapidly with temperature. Information on the subject is limited and, therefore, the cause of the rapid variations with temperature unknown. A satisfactory explanation, however, should include not only the effect of the solvent cage but, also, the variations in the polymolecular structure of the water itself.

Regarding the consistency of the experimental data with x-rays, measurements with conductivity water were found to be invariant with time, whereas, measurements with Barnstead still water were found to vary. In particular, measurements of H\textsubscript{2}O\textsubscript{2} in oxygenated Barnstead still water with ultraviolet radiation were found to vary by as much as 400 percent; in contrast, variations with conductivity water were limited to 10 percent by the sensitivity of the titration method for H\textsubscript{2}O\textsubscript{2}.

Again, Fricke's (Fr34) limited measurements are consistent with Curve III.
in Fig. (II-1) whereas those of Bonet-Maury (Bo48) are found to be at variance. A plausible explanation for this is given in Chapter IV.

III. CALCULATIONS AND DEDUCTIONS

3.1 Kinetics of Radicals. Before proceeding with the analysis of the experimental results, it becomes necessary to establish a mathematical formulation of the kinetics of radicals and molecules in the liquid state. Specifically, the desired form must be consistent with the rate laws and should, preferably, give the average time that it takes for a radical A or B to interact chemically. In general, the average time for a given radical or molecule A to collide with anyone of the B's will be inversely proportional on the concentration of the latter:

$$\tau_{AB} \propto \frac{L/W}{N_B} \quad (\text{II-1a})$$

where $N_B$ is the number of B's in a gram of water, $L$ is Avogadro's number, and $W$ is the molecular weight of water. The constant of proportionality in (II-1a) is the reciprocal of the number of B and water molecules with which A has collided in one second; that is,

$$\text{No. of collisions/sec.} = 8j \quad (\text{II-2})$$

where $j (= 6D_{AB}/\overline{L^2})$ represents the total number of cage-to-cage jumps per second (Po38) that A makes in its zig-zag motion, while the factor of 8 corresponds to the number of new molecules that A encounters at each new cage; $\overline{L^2} (= 10^{-15} \text{ cm}^2)$ corresponds to the square of the mean distance between cages while

$$D_{AB} = D_A + D_B \quad (\text{II-3})$$

corresponds to the effective diffusion coefficient for A and B in water. Therefore, on substitution in (II-1a)

$$\tau_{AB} = \overline{L^2}/48WD_{AB}^2N_B = 10^8/144D_{AB}N_B^2 \quad (\text{II-1b})$$

A similar expression can be set up for the collision time of a B radical or
FIG. II-4

NO. OF $\cdot H_2O_2$'S / GM. OF WATER

NO. OF ION PAIRS / GM. OF WATER

$N_{H_2} = 0$

$N_{H_2} = 15 \times 10^{16}$ $H_2^+$S / GM. $H_2O$
FIG. II-5

DOSAGE $= 0.70 \times 10^{16}$ ION PAIRS / GM. H$_2$O

DOSAGE $= 1.22 \times 10^{16}$ ION PAIRS / GM. H$_2$O

NO. OF H$_2$O$_2$'S / GM. OF H$_2$O

NO. OF H$_2$'S / GM. OF WATER (N$_{H_2}$)

$6 \times 10^{16}$
FIG. II-6

TEMPERATURE °C

RELATIVE YIELD

$N_{H_2} = 19 \times 10^{16}$

$N_{O_2} = 16 \times 10^{16}$
molecule with the $A$'s. Hence for any concentration, the collision time will depend on whether the $A$'s are considered to collide with the $B$'s or the $B$'s with the $A$'s. The resolution of the proper collision time will depend on the particular problem under consideration. In general,

$$\tau_{A,B} = \frac{11^2/45D_{AB}N_{AB}}{10^8/144D_{AB}N_{AB}} = \frac{11^2}{10^8}$$

(II-4)

where $N_{AB}$ is equal to $N_A$ or $N_B$.

The important quantity, however, is the time that it takes $A$ and $B$ to interact chemically. Hence, the average lifetime for an $A$ or a $B$ is

$$\tau_{A+B} = \frac{\tau_{A,B}}{\xi_{A,B}}$$

(II-5)

where $\xi_{A,B}$ represents the probability that $A$ and $B$ will interact chemically in a given solvent cage. This formulation of the problem is consistent with the rate law which may be expressed as (CH43, p. 61):

$$\text{No. of chemical interactions/sec.} = \frac{N_{BA}}{\tau_{A+B}}$$

(II-6)

where $N_{BA} = N_A N_B / N_{AB}$.

On occasion it becomes necessary to determine the concentration of a radical $A$ when it interacts mainly with itself (i.e., $\text{OH} + \text{OH} = \text{H}_2\text{O}_2$). This can be determined by assuming that a steady state is established when the rate of the number created equals the rate of those removed by interaction; alternatively, this is equivalent to a complete renewal of the steady state concentration of the $A$'s during the lifetime of the radicals, or

$$n \tau_{A+A} = N_A$$

(II-7)

where $n$ represents the number of free radicals and, therefore, the number of ion-pairs/sec./gm of water. On substituting in (II-5) and assuming that $N_{AB} = N_A$, then
Thus the steady state concentration of the \( A \) radicals depends on the square root of the rate of dosage. Similarly, the expression for the lifetime of the \( A \) radicals may be written as

\[
\tau_{A+A} = \frac{10^8}{\sqrt{144 n D_{AA}} \xi_{A,A}} \tag{II-9}
\]

3.2 The Influence of \( O_2 \) in Irradiated Water. Curves I, II and III in Figs. (II-1) and (II-2) indicate that the initial yield of 0.80 \( H_2O_2 \) molecules per ion-pair is constant for concentrations at least as low as \( 10^{15} \) \( O_2 \) molecules per gram of water. The significance of this statement is great and needs to be interpreted. If it is assumed that the resultant effect of irradiation is the creation of \( H \) and \( OH \) free radicals in water, then the formation of \( H_2O_2 \) can be accounted in part by

\[
OH + OH \longrightarrow H_2O_2 \tag{II-10}
\]

that is, the maximum yield that can be expected from this source is 0.50 \( H_2O_2 \) molecules/ion-pair. This assumes that all the \( H \)-atoms are eliminated from recombining with the \( OH \) by the following reaction:

\[
H + O_2 \longrightarrow HO_2 \tag{II-11}
\]

where the \( HO_2 \) is described as a semistable free radical in which the bond energy for the \( H \)-atom has been estimated to be about 2.5 ev (Da46, We47).

In order to account for the larger observed yield of \( H_2O_2 \), it becomes necessary to consider the possible contributions by the \( HO_2 \). Two possible reactions may be expected to act as a source of \( H_2O_2 \):

\[
H + HO_2 \longrightarrow H_2O_2 \tag{II-12}
\]

and

\[
HO_2 + HO_2 \longrightarrow H_2O_2 + O_2 \tag{II-13}
\]

Both are energetically possible but (II-12) has to be discarded, chiefly, because the initial yield is independent of the concentration of \( O_2 \); that is, with high \( O_2 \) concentrations, the \( H \)-atom is more likely to interact with \( O_2 \) than with the
much smaller concentration of H\textsubscript{2}O\textsubscript{2}'s (see Sec. 3.7).

If both (II-10) and (II-13) contribute to the H\textsubscript{2}O\textsubscript{2} formation, then the initial rate of yield should be 1.0 instead of 0.80. The possibility that

\[
H + \text{OH} \rightarrow \text{HOH}
\]  

(II-14)

can account for the difference is untenable. The reason reverts, again to the constancy of the initial yield for concentrations of O\textsubscript{2} which are as low as \(10^{15}\) molecules/gm of water. Consequently, to remedy the situation, it becomes necessary to assume that

\[
\text{OH} + \text{HO}_{2} \rightarrow \text{HOH} + \text{O}_{2}
\]  

(II-15)

Thus, initially, one O\textsubscript{2} molecule is absorbed for every two molecules of H\textsubscript{2}O\textsubscript{2} that is formed. As soon as back reactions become prominent, the net O\textsubscript{2} absorption decreases rapidly so that the amount that is converted into H\textsubscript{2}O\textsubscript{2} is small. This agrees quite well with experimental observations since the absorption of oxygen was barely perceptible.

If the region at which the formation of H\textsubscript{2}O\textsubscript{2} is comparable to the number of water molecules formed by the recombination of \(H\) and \(\text{OH}\) free radicals was known, then, it would be a simple matter to determine the probability of capture for reaction (II-11) while in a solvent cage. Since this region lies below the limit of H\textsubscript{2}O\textsubscript{2} detection, then, only an upper limit can be estimated. Thus the relative lifetime of the H-atom may be expressed as follows: (refer to Eq. II-5)

\[
| \frac{\tau_{\text{H+OH}}}{\tau_{\text{H+O}_{2}}} | = \frac{N_{\text{O}_{2}}}{N_{\text{OH}} \cdot \frac{S_{\text{H,O}_{2}}}{S_{\text{H,OH}}}}
\]  

(II-16)

where \(D_{\text{OH}}\) is assumed to be equal to \(D_{\text{O}_{2}}\) (= 2 \times 10^{-5} \text{ cm}^{2}/\text{sec.}) The OH concentration is unknown but it can be estimated, approximately, with the aid of Eq. (II-8) where \(n = 29 \times 10^{12} \text{ ion-pairs/sec.}/\text{gm of water.}\) Hence

\[
N_{\text{OH}} = 70 \times 10^{10} \sqrt{S_{\text{OH,OH}}^{1/2}} \text{ OH's/gm H}_{2}\text{O}
\]  

(II-17)
On substituting and solving for the probability of capture

$$\xi_{H_2O_2} < \frac{1}{1400} \frac{\xi_{H_2}O\text{H}}{\xi_{OH,OH}^{1/2}}$$  \hspace{1cm} (II-18)

To a first approximation the values of \(\xi_{H_2}O\text{H}\) and \(\xi_{OH,OH}\) may be assumed to be unity (see Sec. 3.2 in Part I).

3.3 The Steady State in \(O_2\) Curves. With oxygen only dissolved in water, the formation of \(H_2O_2\) reaches a steady state that equals, approximately, the concentration of \(O_2\). As already explained in the previous section, the absence of \(O_2\) cannot be used to account for this phenomenon. An explanation based on the interaction of the \(OH\) free radicals with \(H_2O_2's\) is equally unsatisfactory. Such an interaction can be used to account for the reduced rate of \(H_2O_2\) formation at concentrations below the steady state but not the drastic change required at the knee of the curve.

An interaction based on the decomposition of \(H_2O_2\) by \(H\)-atoms should fare no better than the \(OH\) interaction unless consideration is given to the competition between the \(O_2's\) and the \(H_2O_2's\) for the \(H\)-atoms. If this affinity for the \(H\)-atom is, approximately, equal for both of them, the explanation for the existence of the steady state becomes obvious.

The \(H\)-atom interacts with \(H_2O_2\) in one of two possible ways:

$$H + H_2O_2 \rightarrow HOH + OH$$  \hspace{1cm} (II-19)

$$\quad \rightarrow H_2 + HO_2$$  \hspace{1cm} (II-20)

Thus the destruction of one \(H\)-atom and one \(H_2O_2\) molecule is equivalent to the creation of an \(OH\) or an \(HO_2\) free radical. Hence the net \(H_2O_2\) decomposition per ion-pair is essentially zero since these radicals will, most likely, recombine to form \(H_2O_2\).

The theory given so far accounts for the levelling off process but does not explain why the \(H_2O_2\) steady state value does not vary linearly with the \(O_2\) concentration. In order to account for this observation, it becomes necessary to assume
that the OH interacts with the H₂O₂ to a small degree. This will be discussed further in connection with the shape of the O₂ curves.

The relative affinity of O₂ and H₂O₂ for the H-atom can be determined from Curve II in Figs. (II-1) and (II-2). This curve is chosen in particular in order to avoid the large probable errors of Curve I and the effect of additional complicating reactions in Curve III. Consider a point on Curve II corresponding to a dosage of 2 x 10¹⁶ ion-pairs/gm of water. This is characterized by

\[ N_{H₂O₂} = 10^{16} \text{H}_2\text{O}_2's/\text{gm of water} \]

and a rate of \( (M/N)_{H₂O₂} = 0.22 \text{H}_2\text{O}_2's/\text{ion-pair} \).

At the same H₂O₂ concentration, Curve III gives a rate of \( (M/N)_{H₂O₂} = 0.60 \text{H}_2\text{O}_2's/\text{ion-pair} \).

That is, in Curve III practically all the H-atoms are absorbed by O₂'s since the latter are 16 times more numerous than the H₂O₂'s. Therefore, the difference in the rates of 0.60-0.22 = 0.38 H₂O₂'s/ion-pair must be accounted, approximately, by the decomposition of H₂O₂'s by H-atoms. As a result, 38 percent of the H-atoms combine with the H₂O₂'s and 62 percent with O₂'s. On using Eq. (II-5), this leads to

\[ \frac{\dot{C}_{H*O₂}}{\dot{C}_{H*H₂O₂}} = \frac{38}{62} = \frac{N_{H₂O₂}}{N₂} \frac{\xi_{H,H₂O₂}}{\xi_{H,O₂}} \]  \hspace{1cm} (II-21)

or the relative probabilities of capture

\[ \frac{\xi_{H,H₂O₂}}{\xi_{H,O₂}} = \frac{38}{62} \frac{1.63 \times 10^{16}}{10^{16}} = 1.0 \]  \hspace{1cm} (II-22)

This value was further verified, experimentally, when it was observed that the steady state concentration of H₂O₂ was found to be the same as the O₂ concentration when irradiating an aqueous solution of O₂ and H₂. The concentration of O₂ in the
water was kept constant during the irradiation by shaking the partially filled unit. The justification for this conclusion is given in the following section.

3.4 Aqueous Solutions of H₂ and O₂. The influence of H₂ on the formation of H₂O₂ in the presence of O₂ is exemplified by Curve IV in Figs. (II-1) and (II-2) and Curve V in Fig. (II-2). As already explained, Curve IV is insensitive to higher concentrations of H₂, at least, at lower dosages where the initial yield of 1.20 H₂O₂'s/ion-pair represents the maximum rate of yield to be expected. If the reasoning in Sec. 3.2 is correct, then, this implies that reaction (II-15) no longer exists when large amounts of H₂ are dissolved in water; that is, one of the following reactions must occur in the presence of molecular hydrogen:

\[ \text{H}_2 + \text{H}_2 \rightarrow \text{HOH} + \text{OH} \]  
\[ \text{OH} + \text{H}_2 \rightarrow \text{HOH} + \text{H} \]  

Thus either the H₂O₂'s are converted into OH free radicals or the OH's into H-atoms and then into H₂O₂'s. Reaction (II-24) is known to be a very slow reaction ([141], p. 303) but nothing is known about (II-23). Information discussed so far gives no hint as to the probable choice. The discussion in the next section, however, definitely favors reaction (II-24).

The initial rate of H₂O₂ formation in the presence of hydrogen is greater than 1.0 and, therefore, greater than can be accounted for by the free radicals created through ion-pair formation. Experiments, however, with non-ionizing radiation and the extreme ultraviolet, in particular, indicate that free radicals can also be formed by this means. Thus a yield greater than 1.0 is not unexpected since more than half of the energy lost by ionizing radiation goes into excitation rather than ionization. It is possible, however, a portion of this excess H₂O₂ can be accounted by a re-evaluation of an ion-pair in the liquid state; that is, the energy loss corresponding to an ion-pair is likely to be less than 32.5 ev and, therefore, a somewhat larger number of ion-pairs than would be predicted by measurements in the
In Curve V of Fig. (II-2), the conversion of OH's by reaction (II-24) into H-atoms is only partially complete. The initial rate of yield for this curve is 0.95 H₂O₂'s/ion-pair compared to 0.80 for the oxygen curves and 1.20 for Curve IV. Consequently, the fraction of the OH's combining to form H₂O₂ for Curve V is probably one-half or less. Assume, however, that its actual value is \( K \). Then the relative fraction of the OH's going into reactions (II-24) and (II-10) will be inversely proportional to the relative lifetimes of the OH's in these reactions, or

\[
\frac{\tau_{OH+H_2}}{\tau_{OH+OH}} = \frac{K}{1-K} = \frac{D_{OH,H_2}}{D_{OH,OH}} \frac{N_{OH/2}}{\xi_{OH,OH}} \frac{\xi_{OH,H_2}}{\xi_{OH,OH}} \tag{II-25}
\]

Assuming Eq. (II-17) for \( N_{OH} \), \( N_{H_2} = 3.2 \times 10^{16} \) molecules/gm of water and \( D_{H_2} = 5 \times 10^{-5} \) cm²/sec, then

\[
\frac{\xi_{OH,H_2}}{\xi_{OH,OH}} = \frac{1}{1-K} \cdot 160,000 \tag{II-26}
\]

Thus a value of 1/160,000 is indicated if \( K = 1/2 \).

3.5 Aqueous Solutions of \( H_2 \) and \( H_2O_2 \). Curves I, II and III of Fig. (II-3) illustrate the effect of x-rays on an air-free aqueous solution of \( H_2O_2 \). These curves furnish no additional information but have been very useful in verifying the hypotheses already suggested. In order to account for the decrease in the initial rate of decomposition at lower concentrations of \( H_2O_2 \), it is only necessary to consider the affinity of the \( H_2O_2 \) for the \( H \) and \( OH \) free radicals. Sections 3.2 and 3.3 indicate that all the \( H \)-atoms go into the decomposition of \( H_2O_2 \) through reactions (II-19) and (II-20). On the other hand, the interaction of \( OH \) with \( H_2O_2 \)

\[
OH + H_2O_2 \rightarrow HOH + HO_2 \tag{II-27}
\]

is very slow unless the \( H_2O_2 \) concentration is very high. Thus at lower concentrations of \( H_2O_2 \), most of the \( OH \)'s may be expected to form \( H_2O_2 \).

The gaseous yield curve in Fig. (II-3) is interesting in that the initial
yield corresponds, approximately, to $1/3 \text{H}_2\text{O}_2$/ion-pair. Thus reaction (II-20) is somewhat less probable than (II-19). This observation is not unexpected since the HO-\text{OH} bond energy in H$_2$O$_2$ (Ho48) is, approximately, half the HOO-H bond energy (We47). A more interesting observation is the absence of a considerable amount of O$_2$ in the gaseous state; that is, the basic process of H$_2$O$_2$ decomposition demands that

$$2 \text{H}_2\text{O}_2 \rightarrow 2\text{HOH} + \text{O}_2 \quad (\text{II-28})$$

The amount of O$_2$ that has been observed is, approximately, 30 percent less than would be expected from (II-28). This contradiction is discussed in greater detail in Part I.

On introducing H$_2$ into an aqueous solution of H$_2$O$_2$, as in Figs. (II-4) and (II-5), the rate of decomposition rises sharply to several H$_2$O$_2$'s per ion-pair. The explanation of this phenomenon must lie in some highly reactive and regenerative process. The \text{OH} radical has been shown to be very slow and, therefore, the chain reaction must involve the regeneration of the H-atoms. Such a process is furnished by

$$\text{H} + \text{H}_2\text{O}_2 \rightarrow \text{HOH} + \text{OH} \quad (\text{II-19})$$

$$\text{OH} + \text{H}_2 \rightarrow \text{HOH} + \text{H} \quad (\text{II-24})$$

The only limitation to this explosive process is reaction (II-20) which serves to prevent the complete destruction of all the H$_2$O$_2$'s by a single H-atom.

3.6 Analysis of Curves. A mathematical formulation of the experimental curves is a tedious process since several reactions take place simultaneously and in a degree which is difficult to determine exactly. However, an attempt will be made to establish such a formulation with the ulterior aim of determining $\xi_{\text{OH}, \text{H}_2\text{O}_2}$.

Curve IV of Fig. (II-1) is characterized by the fact that practically all the \text{OH}'s are converted into H-atoms by molecular hydrogen. Therefore, the H$_2$O$_2$ yield will be limited by the relative concentration of O$_2$ and H$_2$O$_2$ since both of them have an equal affinity for the H-atom. Mathematically, the rate of H$_2$O$_2$
yield may be expressed in terms of the dosage N as

\[ \frac{dN_{H_2O_2}}{dN} = \left( \frac{M}{N} \right)_{H_2O_2} \left[ 1 - \frac{\tau_{H_2O_2}}{\tau_{H_2O}} \right] \]  

(II-28)

where \( \left( \frac{M}{N} \right)_{H_2O_2} \) represents the initial rate of \( H_2O_2 \) yield per ion-pair. On substituting and integrating

\[ N_{H_2O_2} = N_{O_2} \frac{\xi_{H_2O_2}}{\xi_{H, H_2O_2}} \left[ 1 - e^{-\left( \frac{M}{N} \right)_{H_2O_2} N_{O_2} \frac{\xi_{H_2O_2}}{\xi_{H, O_2}}} \right] \]  

(II-29)

This equation is a good approximation for Curve IV of Fig. (II-1) only at low dosages where the \( O_2 \) concentration may be considered to be constant. For a better agreement at higher dosages, Eq. (II-28) should be integrated to include the assumption that one \( O_2 \) molecule is absorbed whenever one \( H_2O_2 \) molecule is formed.

The form of Eq. (II-29), however, is satisfactory for Curve III of Fig. (II-1) where the \( O_2 \) concentration remains essentially constant. However, an additional term must be introduced to express the interaction of \( OH \) with \( H_2O_2 \). The final form of the equation may be expressed as follows:

\[ N_{H_2O_2} = N_{O_2} \left[ 1 - e^{-\left( \frac{M}{N} \right)_{H_2O_2} \left( \frac{N}{N_{O_2}} \frac{\xi_{H_2O_2}}{\xi_{H, O_2}} + \frac{2N}{N_{OH}} \frac{\xi_{H_2O_2}}{\xi_{OH}} + \frac{\xi_{O_2}}{\xi_{OH}} \right)} \right] \]  

(II-30)

A good fit was obtained at low dosages with

\[ \frac{\xi_{OH, H_2O_2}}{\xi_{OH, OH}}^{1/2} = 1/200,000 \]  

(II-31)

The value found at higher dosages was smaller so that at the steady state portion of the curve it had a value of 1/450,000. There are two reasons why the value of the probability of capture appears to decrease with dosage: first, the assumption that \( \left( \frac{M}{N} \right)_{H_2O_2} = 0.80 \) \( H_2O_2 \) 's/ion-pair is an approximation since it depends on the relative concentration of the \( OH \) and the \( H_2O_2 \); second, the effect of the \( H_2 \) given
by reaction (II-20) was not included in the formulation since it is difficult to evaluate and, also, because it is not an important factor at low dosages.

3.7 Lifetime and Range of Radicals. The mean lifetime of the free radicals created by radiation in water can be determined with the aid of Eq. (II-6) or Eq. (II-9). It is obvious from these equations that the lifetime is not a fixed quantity but dependent on the concentration of the solute and the rate of dosage. Once the lifetime of a radical has been established, then its range can be determined with the aid of Einstein’s Displacement Law:

$$\sqrt{\frac{x^2}{n}} = \sqrt{2D t} \quad (II-32)$$

That is, the root mean square distance travelled by a particle depends on both the diffusion coefficient D and the time t.

Since no reaction was found that could give any direct information on the properties of the HO₂, a number of experiments were attempted to determine whether it had a long lifetime. The results were negative, at least, for a lifetime greater than 15 seconds. Assuming it had a lifetime of one second, then according to Eq. (II-9) $\xi_{HO₂,HO₂} = 1/1700$ for $n = 29 \times 10^{12}$ ion-pairs/gm of water and $D_{HO₂} = 2 \times 10^{-5}$ cm²/sec. This value appears to be too small and should be nearer unity. The reasoning behind this hypothesis is not materially different from that used in assuming that the probability of interaction between two OH radicals should be close to unity while in a solvent cage (see Part I). Additional confirmation for this is provided, indirectly, by the uniform prominence of reactions (II-10), (II-13) and (II-15) in describing the behavior of the oxygen curves.

IV. CONCLUSIONS

The original hypothesis of Weiss, Lea and Burton that H and OH free radicals are created in water in the presence of radiation, has been assumed to be fundamentally correct. As a result, analysis of the experimental data, in this light,
has been fruitful rather than contradictory. In general, a simple and satisfactory theory has been established with the probability of capture while in a solvent cage being the outstanding property for any given reaction. Analysis of theoretical and experimental data suggests that the probability of capture may be subdivided into three distinct groups:

**Radical-Radical Interactions**

\[
\begin{align*}
H + H &\rightarrow H_2 & \xi_{H,H} &= 1 \\
H + OH &\rightarrow HOH & \xi_{H,OH} &= 1 \\
OH + OH &\rightarrow H_2O_2 & \xi_{OH,OH} &\leq 1 \\
HO_2 + HO_2 &\rightarrow H_2O_2 + O_2 & \xi_{HO_2,HO_2} &< 1 \\
HO_2 + OH &\rightarrow HOH + O_2 & \xi_{OH,HO_2} &< 1
\end{align*}
\]

**H-atom - Molecule Interactions**

\[
\begin{align*}
H + O_2 &\rightarrow HO_2 \\
H + H_2O_2 &\rightarrow HOH + OH & \xi_{H,O_2} = \xi_{H,H_2O_2} \leq \frac{1}{1400} \frac{\xi_{H,OH}}{\xi_{OH,OH}} \\
&\rightarrow H_2 + HO_2
\end{align*}
\]

**OH-radical - Molecule Interactions**

\[
\begin{align*}
OH + H_2O_2 &\rightarrow HOH + HO_2 & \xi_{OH,H_2O_2} = \xi^{1/2}_{OH,OH}/200,000 \\
OH + H_2 &\rightarrow HOH + H & \xi_{OH,H_2} = \xi^{1/2}_{OH,OH}/160,000
\end{align*}
\]

This arrangement suggests that the probability of capture in a solvent cage is independent, to a first approximation, of the solute and depends only on the type of radical with which it interacts: H, OH, or HO_2. The rejection of reaction (II-23) in preference to (II-24) indicates that the reactivity of the HO_2 free radical is considerably less than that for the OH.

The value of \( \xi_{H,O_2} \) and \( \xi_{H,H_2O_2} \) has been assumed to be given, approximately, by Eq. (II-18). This is justified by the close agreement between the experimental
and theoretical results for air-free water in Section 3.2 of Part I.

Use of the usual rate constant to express the properties of a reaction has been avoided, intentionally, since it was felt that a clearer presentation can be made if emphasis is placed on the probability of capture for a given reaction. However, for convenience, the rate constant may be determined from Section 3.1 as

\[ k_{AB} = (48WD_{AB} \xi_{AB}/\text{Li}^2)(\text{L}/10^3) = 0.86 \times 10^{15}D_{AB} \xi_{AB} \]  

(II-33)
in terms of moles/liter.

It was noted on page 29 that Fricke's measurements (Fr34) with O₂ dissolved in water were consistent with the curves in Fig. (II-1), whereas, those of Bonet-Maury (Bo48) show deviations that need to be explained: (a) a low initial rate of yield of 0.57 \( \text{H}_2\text{O}_2 \)'s/ion-pair and (b) a steady state in which \( \text{N}_\text{H}_2\text{O}_2 > \text{N}_\text{O}_2 \) rather than equal, approximately. According to the deductions already made, such a situation can only exist in the absence of H-atoms or in an excess of OH radicals. Since Bonet-Maury used 4 angstrom x-rays wherein the surface penetration is a small fraction of a millimeter, then the escape of a portion of the H-atoms into the adjoining space or medium appears to be a reasonable explanation of the observed differences.

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