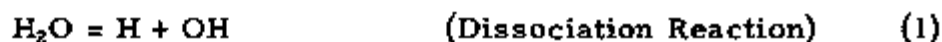## 2.2   Effect of Ionizing Radiations on Liquids (S. Gordon, E. J. Hart, P. Walsh)

2.2.1   Effect of the Type of Radiation on Dissociation and Recombination Reactions in Aqueous Solutions

Two means have been developed for studying the effect of the type of radiation on dissociation and recombination reactions in aqueous solutions. One method based on an analysis of the products of the formic acid-oxygen reaction was described in the previous quarterly report.[1] This method has been extended to a comparison of the effects of Co^{60} gamma rays and tritium beta rays on water. A second method is based on the ratio of ferrous sulfate oxidation in the presence and absence of air. This method has been applied to a study of the effects of Co^{60} gamma rays, mixed pile radiation, and the products of the $B^{10}(n, \alpha)$ reaction. The details of these experiments are described below.

Oxidation of Formic Acid by Co^{60} Gamma Rays and Tritium Beta Rays   The course of oxidation of formic acid may be represented by the following reactions:

$$H_2O = H + OH \qquad \text{(Dissociation Reaction)} \qquad (1)$$

$$H_2O = 1/2\ H_2 + 1/2\ H_2O_2 \qquad \text{(Recombination Reaction)} \qquad (2)$$

$$OH + HCOOH = H_2O + HCOO \qquad\qquad\qquad (3)$$

$$H + HCOOH = H_2 + HCOO \qquad\qquad\qquad (4)$$

$$H + O_2 = HO_2 \qquad\qquad\qquad (5)$$

$$HCOO + H_2O_2 = H_2O + CO_2 + OH \qquad\qquad\qquad (6)$$

$$HCOO + O_2 = HO_2 + CO_2 \qquad\qquad\qquad (7)$$

$$HO_2 + HO_2 = H_2O_2 + O_2 \qquad\qquad\qquad (8)$$

$$HCOO + OH = H_2O + CO_2 \qquad\qquad\qquad (9)$$

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[1]ANL-4564, section 2.1.1.

The passage of ionizing radiations through aqueous solutions gives rise to the formation of hydrogen and hydroxyl free radicals. At the end of electron tracks or in regions of high ionization density, the free radical concentration becomes high and pairwise recombination (reaction (2)) becomes highly probable. In the above scheme, reaction (1) does not represent the total number of water molecules undergoing dissociation by the radiation, but only the number of hydrogen and hydroxyl radicals that escape recombination in reaction (2) or in the reaction H + OH = H_2O. Since reaction (2) occurs in regions of high free radical concentration, this recombination step is rapid and the reaction possesses the characteristics of a primary one. Reaction (1) is termed the dissociation reaction and reaction (2) the recombination reaction. Reactions (3) and (6) represent the chain propagation steps. (4) and (5) are the competitive steps for hydrogen atom consumption, and (8) and (9) are the chain termination steps.

In the previous experiments[1] with Co^{60} gamma rays, it was found possible to suppress reaction (4) by maintaining an oxygen concentration of 1.24 mM. Under these conditions hydrogen formation is due entirely to reaction (2) and oxygen consumption is a measure of reaction (1). From the data reported previously,[1] it is found that the following equation holds for the rate of hydrogen formation in 0.01 M formic acid solutions:

$$\frac{dH_2}{dt} = k_2 + \frac{k_1}{1 + 38.7(O_2)}.$$

In the above equation k_1 is the rate constant for the dissociation reaction and k_2 is the rate constant for the recombination reaction. These constants have been measured for the beta rays from tritium disintegration in 0.01 M formic acid containing 1.24 mM oxygen. At an activity of 157 curies of tritium per liter, the oxidation of formic acid is rapid enough so that the thermal decomposition of hydrogen peroxide is not very pronounced. The data obtained appear in Figure 13. From the data of Figure 13 the constants k_1 and k_2 are found to be 4.64 and 2.01 mM radical pairs per liter per hour, respectively. Therefore 30% of the radical pairs formed recombine according to equation (2) and 70% react with formic acid and oxygen. The results for tritium beta rays and Co^{60} gamma rays are summarized in Table IX. From this table it is observed that the reduction in the energy of the electron from 500,000 ev to 5690 ev increases the percent of radicals recombining from 21 to 30% of the total number formed.
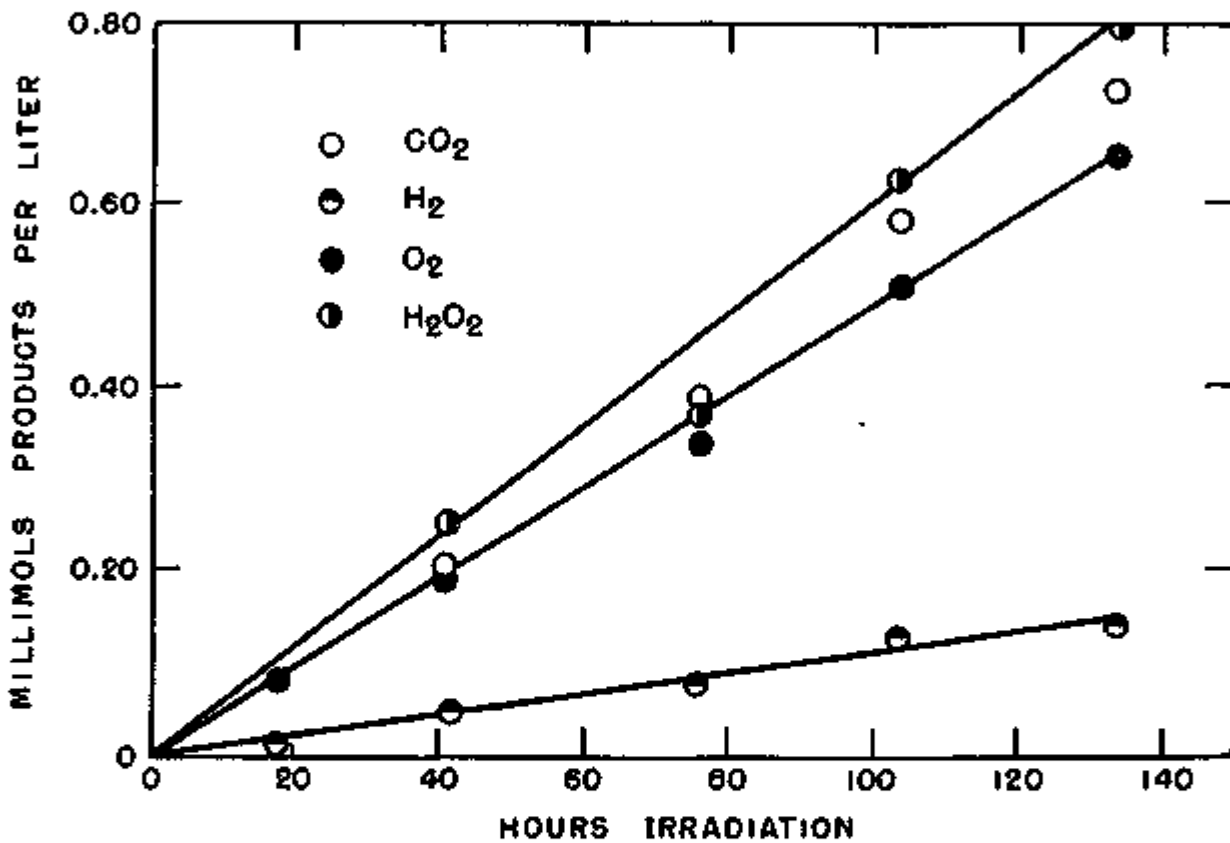
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[1]ANL-4564, section 2.1.1.

FIGURE 13.

OXIDATION OF 0.01 $\underline{M}$ FORMIC ACID PLUS 1.24 $\underline{mM}$
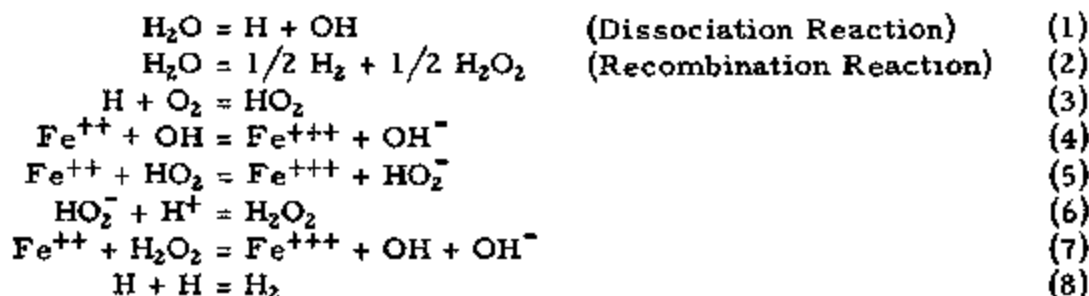OXYGEN BY TRITIUM DISINTEGRATION AT 157 CURIES PER LITER.

TABLE IX

Effect of Type of Ionizing Radiations on Dissociation and
Recombination Reactions in 0.01 $\underline{M}$ Formic Acid Solutions

Radiation	Percent Radicals Involved in	
	Dissociation (Reaction (1))	Recombination (Reaction (2))
Co^{60} Gamma Rays	79	21
Tritium Beta Rays	70	30

Since tritium undergoes beta decay to form He^3 with a 12.46-yr half-life and a mean energy of 5690 ev, it is possible to calculate the energy expended per radical pair formed from the above data. At an activity level of 157 curies per liter the energy absorption amounts to 1.19×10^{20} ev per liter per hour. Since 6.65×10^{-6} moles of radical pairs per liter per hour are produced, an average energy of 29.8 ev per measurable radical pair is expended in aqueous solutions of formic acid. If it is assumed that 13 ev are required for ionization of water to H_2O^+, an additional 17 ev of energy in the secondary electron are necessary on the average for formation of the radical pair in aqueous formic acid solutions.

Oxidation of Ferrous Sulfate Solution by Co^{60} Gamma Rays, Pile Radiation and the Products of the (n, α) Reaction on B^{10}. The mechanism for the radiation induced oxidation of ferrous sulfate is considered to be the following:

$$H_2O = H + OH \qquad \text{(Dissociation Reaction)} \qquad (1)$$
$$H_2O = 1/2\ H_2 + 1/2\ H_2O_2 \qquad \text{(Recombination Reaction)} \qquad (2)$$
$$H + O_2 = HO_2 \qquad (3)$$
$$Fe^{++} + OH = Fe^{+++} + OH^- \qquad (4)$$
$$Fe^{++} + HO_2 = Fe^{+++} + HO_2^- \qquad (5)$$
$$HO_2^- + H^+ = H_2O_2 \qquad (6)$$
$$Fe^{++} + H_2O_2 = Fe^{+++} + OH + OH^- \qquad (7)$$
$$H + H = H_2 \qquad (8)$$

In the absence of air the oxidation follows reactions (1), (2), (4), (7), and (8). In the presence of air, reactions (1) through (7) inclusive are followed. Therefore reaction (1) leads to the oxidation

of four ferrous ions in the presence of oxygen and one ferrous ion in the absence of oxygen, whereas but one ferrous ion is oxidized per water molecule dissociated in reaction (2) whether oxygen is present or not.

Let $\underline{x}$ be the fraction of total water molecules dissociated involved in reaction (1), and $1-x$ the fraction involved in reaction (2). Then the yield ratio, $Fe_{O_2}^{+++}/Fe_{vac.}^{+++} = \dfrac{4x + (1-x)}{x + 1 - x} = 3x + 1$. Therefore, the fraction of water molecules dissociated involved in reactions (1) and (2) may be calculated from measurements of ferrous sulfate oxidation in the presence and absence of air.

Table X contains a comparison of results employing 1 $\underline{mN}$ ferrous sulfate in 0.8 $\underline{N}$ sulfuric acid. The types of radiations studied were Co^{60} gamma rays, mixed gamma and neutron radiation in CP-3´ and the products resulting from B^{10} disintegration in the pile. In the latter case the ferrous sulfate solutions were made 75 $\underline{mM}$ in boric acid. The boric acid showed no detectable effect on oxidation of ferrous sulfate in the presence or absence of air when irradiated with Co^{60} gamma rays. Therefore, it is assumed that the increased oxidation of ferrous sulfate containing boric acid is due to the $B^{10}(n, \alpha)Li^7$ reaction. Table X shows the expected trend, namely, that the percent of recombination according to reaction (2) increases as the proportion of heavy particle radiation increases.

TABLE X

Effect of Type of Ionizing Radiations on Dissociation and Recombination Reactions in 1 $\underline{mN}$ Ferrous Sulfate Solutions

Radiation	Percent Radicals Involved in	
	Dissociation (Reaction (1))	Recombination (Reaction (2))
Co^{60} Gamma Rays	35	65
CP-3´ Radiation	25	75
CP-3´ Radiation plus $B^{10}(n, \alpha)Li^7$	13	87
$B^{10}(n, \alpha)Li^7$	8	92

A comparison of the formic acid and the ferrous sulfate methods for determining the fraction of radicals formed in reactions (1) and (2) may be made for the case of Co^{60} gamma rays. It is observed (Table IX) that the formic acid-oxygen method gives 79 percent of the radicals as being formed in reaction (1) and the ferrous sulfate reaction gives but 35 percent. At present it is not possible to provide a really definitive explanation for this disparity in results. It is known, however, that the ferrous sulfate reaction is very sensitive to certain impurities and it is possible that the presence of these impurities contributes to the difference in results.

2.2.2   Radiation Chemistry of Ferrous Sulfate Solutions

Effect of Dose-Rate   The ferrous sulfate dosimeter is generally considered to have an oxidation rate by ionizing radiations that is independent of dose-rate. Recent work,[1] however, suggested that the ferrous sulfate dosimeter might show this independence of dose-rate only up to a dose-rate of ca. 50 r/sec. If this were true it would not be possible to employ this dosimeter for measuring gamma ray fluxes at the high intensities existing in reactors. Therefore, experiments were carried out to determine the applicability of the dosimeter at the fluxes obtaining in CP-3′.

Hardwick[1] has shown that the radiation induced reduction of ceric sulfate is independent of dose-rate in the range from 2 to 3000 r/sec. Therefore, a measurement of the ratio of ceric ion reduction to ferrous ion oxidation under conditions where the dose-rate is varied should establish the behavior of the ferrous sulfate system. If this ratio remains independent of dose-rate, then it is proved that the ferrous sulfate oxidation is also independent of dose-rate. Table XI gives the results obtained for dose-rate variations from 0.36 to 350 r/sec as obtained from the Co^{60} gamma source and CP-3′. No variation within the limits of experimental error is observed in this dosage range.

Effect of Formic Acid   The effect of formic acid on the oxidation of ferrous sulfate is being studied in order to measure the effect produced by organic impurities on this reaction. This is important, as mentioned previously, in measuring relative amounts of the dissociation and recombination reactions (see section 2.2.1). The ratio $Fe_{air}^{+++}/Fe_{vac}^{+++}$ has been found to be highly dependent on the manner in which the ferrous sulfate solutions are evacuated.

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[1]T. J. Hardwick, private communication.

TABLE XI

Effect of Dose-Rate on Reduction of Ceric Sulfate and Oxidation of Ferrous Sulfate in 0.8 $\underline{N}$ Sulfuric Acid

Radiation	Dose-Rate (r/sec)	Ce^{+3} Formed ($\mu N/\ell/min$)	Fe^{+3} Formed ($\mu N/\ell/min$)	Fe^{+3}/Ce^{+3} Ratio
Co^{60} Gamma Rays	0.36	0.056	0.377	6.7
"	13.2	2.04	13.9	6.8
CP-3'	350	45	316	7.0

Ratios varying from 2.0 to 19.0 have been reported.[1] Table XII gives the effect of formic acid in the range from zero to 10 $\underline{mM}$ on the oxidation of ferrous sulfate in 0.8 $\underline{N}$ sulfuric acid. The ratio is observed to vary from 2.04 to infinity as the concentration of formic acid is increased to 10 $\underline{mM}$ per liter. Thus formic acid increases the rate of oxidation of ferrous sulfate in the presence of oxygen. Removal of oxygen leads to the complete suppression of the ferrous sulfate oxidation in the presence of formic acid. On this basis it is possible that the lower the ratio, the freer the solution is of organic impurities.

TABLE XII

Effect of Formic Acid on the Radiation-Induced Oxidation of Ferrous Sulfate in 0.8 $\underline{N}$ Sulfuric Acid in the Presence and Absence of Oxygen
(Dose-rate of 50,000 r/hr from the Co^{60} gamma source)

$FeSO_4$ Conc. (mN/ℓ)	HCOOH Conc. (mN/ℓ)	Fe^{+3} Formed ($\mu N/\ell/hr$)		Ratio $Fe^{+++}_{air}/Fe^{+++}_{vac}$
		Air Free	Air Sat.	
1.0	0.0	440	900	2.04
0.5	1.0	250	1100	4.48
0.5	10.0	0.0	>2400	∞

[1]ANL-4526, section 2.2.3.

Further work on the effect of 0.1 $\underline{M}$ and 1.0 $\underline{M}$ formic acid shows that the initial rate of oxidation of ferrous sulfate is increased up to 15-fold over the rate found in the absence of formic acid. Work is being continued on the effect of formic acid and oxygen on this reaction for the purpose of developing a more sensitive chemical dosimeter than is at present available.

2.2.3 Gamma Ray Induced Reaction of Deuterium Gas with Liquid Water

Several additional scouting experiments have been carried out in connection with the gamma ray induced exchange between deuterium gas and liquid water.[1] An attempt was made to establish whether a dependence on deuterium concentration and on radiation intensity existed. For one set of samples deuterium gas was dissolved in water under a pressure of 23.0 cm of deuterium, the concentration of deuterium at this pressure being 356.0 μmoles/liter. Another set of samples was prepared in which the deuterium was dissolved under a pressure of 67.5 cm giving a concentration of 759 μmoles/liter of deuterium. Both sets of samples were exposed under identical conditions to the Co^{60} gamma ray source at a radiation intensity of 18,500 r/hr. Samples from each set were analyzed alternately. The results of the mass spectrometric analyses of the dissolved gas are plotted in Figure 14. The initial rate of production of HD is 4.8 and 3.8 μmoles/liter/1000 r at the initial deuterium concentrations of 356 and 759 μmoles/liter, respectively. This difference is beyond experimental error. The greater initial rate of production of HD at the lower concentration is hard to understand. It is possible that an impurity is playing a role. This will be checked further.

One run was made to check the effect of radiation intensity on the yield. A set of samples containing a concentration of 684 μmoles/liter of deuterium was exposed at a dose-rate of 1550 r/hr. The results are also shown in Figure 14. At this dose-rate the yield of HD was 5.2 μmoles/liter/1000 r, as compared to a yield of 3.3 μmoles/liter/1000 r at initial deuterium concentrations of 691 μmoles/liter. Whether this is real or again due to impurities will also be checked.

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[1]See ANL-4564, section 2.2.3 and ANL-4526, section 2.2.1 for previous results.
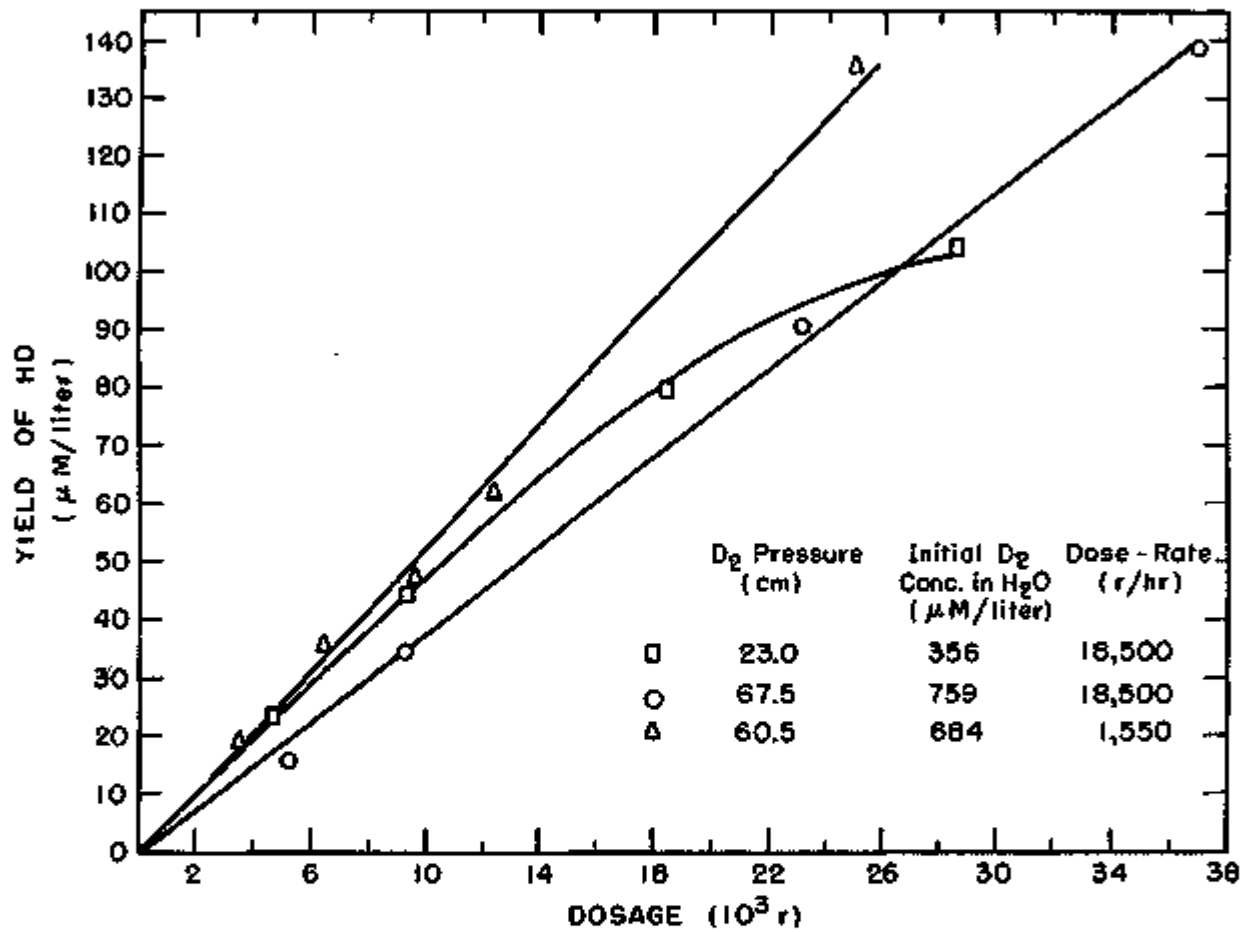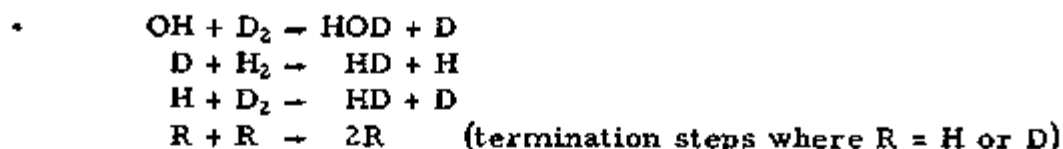
FIGURE 14.

EFFECT OF DEUTERIUM CONCENTRATION AND DOSE-RATE
ON THE GAMMA RAY INDUCED ISOTOPIC EXCHANGE
BETWEEN DEUTERIUM GAS AND LIQUID WATER.

An attempt was made to see whether a chain could be set up according to the following scheme:

$$OH + D_2 \rightarrow HOD + D$$
$$D + H_2 \rightarrow HD + H$$
$$H + D_2 \rightarrow HD + D$$
$$R + R \rightarrow 2R \quad \text{(termination steps where R = H or D)}$$

A run was made with a mixture of equal amounts of hydrogen and deuterium at a total concentration of $607\,\mu$moles/liter. The results are shown in Figure 15. The initial yield of HD is about $12.5\,\mu$moles/liter/1000 r. This indicates the possibility of a chain reaction and we are repeating this experiment at a lower radiation intensity.

One run which was made but not reported previously was designed to check the effect of adding ferrous sulfate on the exchange. The presence of ferrous sulfate might suppress the effect of OH radicals in the D_2 reaction due to the fast reaction of OH with Fe^{++}. In this run very little HD was produced, $<1\,\mu$mole/liter/1000 r, but the normal yield for Fe^{++} oxidation and hydrogen production was obtained. This seems to indicate that the OH radical is playing an important role in this reaction. This experiment is being repeated to get additional data.

The results of the various scouting runs are summarized in Table XIII.

TABLE XIII

Production of Hydrogen Deuteride by Gamma Irradiation of Aqueous Solutions Containing Dissolved Deuterium and Hydrogen

| Composition of Aqueous Solution	Gamma Dose-Rate (1000 r/hr)	Initial HD Yield (μM/1000 r)	Remarks
759 μM D_2	18.5	3.8	Departs from linearity at ca. 30,000 r.
356 μM D_2	18.5	4.8	Departs from linearity at ca. 10,000 r.
684 μM D_2	1.55	5.2	Linear to 25,000 r as far as carried.
691 μM D_2	18.5	3.3	Linear to ca. 20,000 r.
607 μM of a 50/50 mixture of D_2 + H_2	18.5	12.5	Linear to ca. 8,000 r.
1 mN $FeSO_4$; 0.8 N H_2SO_4; 858 μM D_2	18.5	<1	Fe^{+++} yield and H_2 yield equal.
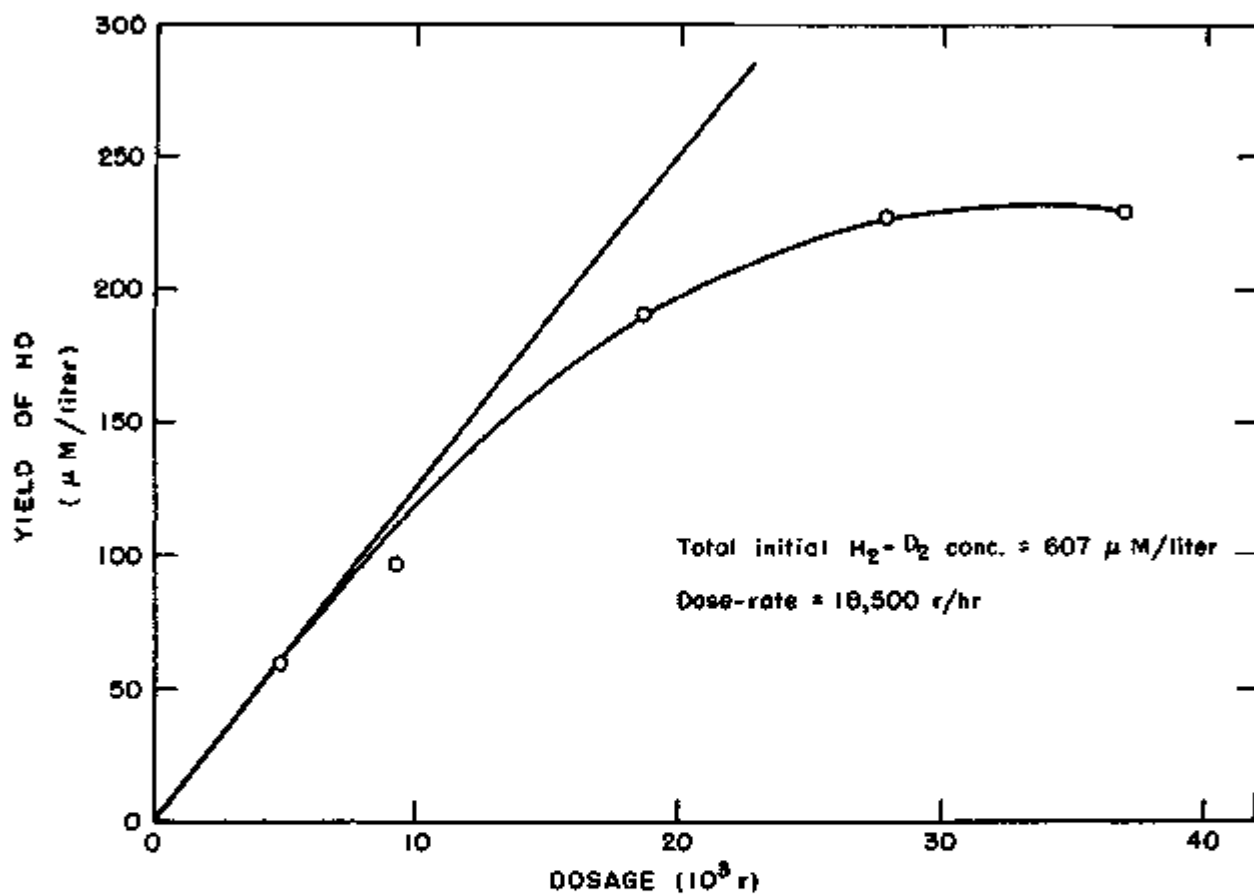
FIGURE 15.

HD FORMATION IN WATER SOLUTION OF EQUAL
MIXTURE OF HYDROGEN AND DEUTERIUM UNDER
GAMMA RAY EXPOSURE.

2.2.4   Application of Oxygen 18 to a Study of the Radiation Induced Water-Oxygen Reaction (with D. Hutchison)

Oxygen 18 is being used to characterize the mode of hydrogen peroxide formation in the gamma ray induced water plus oxygen reaction. Hydrogen peroxide is formed in the recombination reaction (2) discussed in section 2.2.1:

$$H_2O = 1/2 \ H_2 + 1/2 \ H_2O_2 \ . \tag{2}$$

In the presence of oxygen, it is also formed by reaction with hydrogen atoms in the following manner:

$$H_2O = H + OH \qquad \text{(Dissociation Reaction)} \qquad (1)$$
$$H + O_2 = HO_2 \tag{1a}$$
$$HO_2 + HO_2 = H_2O_2 + O_2 \ . \tag{1b}$$

A possible mode of disappearance of the hydroxyl radicals produced in the dissociation reaction is

$$OH + OH = H_2O + 1/2 \ O_2 \ . \tag{2a}$$
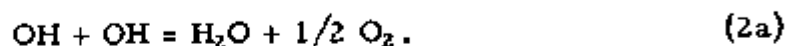
If this occurs, normal oxygen liberated directly from the water would increase the ratio O^{16}/O^{18} in the dissolved oxygen.

Oxygen 18 was added to air-free water and irradiated with Co^{60} gamma rays. After irradiation the dissolved oxygen in the samples was collected. The de-oxygenated solutions were then treated with air-free ceric sulfate in order to liberate oxygen from the hydrogen peroxide. Mass spectrometer analysis of these two types of samples was then carried out. While the experimental error was larger than desirable, results showed that the O^{18} content of the dissolved oxygen did not change during irradiation. This indicates that reaction (2a) does not play a significant role. However, the O^{18} content of the oxygen liberated from the hydrogen peroxide was lower than that of the O^{18} added to the solution but not as low as the O^{18} content of normal water. This indicates that hydrogen peroxide is formed through reactions (1), (1a), and (1b) from the dissolved oxygen as well as from the recombination reaction (2).

The O^{18} content of the oxygen in the hydrogen peroxide is independent of time of irradiation from 3 to 16 hours. From the results obtained it is deduced that 25 percent of the hydrogen peroxide formed is contributed by the recombination reaction (2). These results were obtained by using enriched oxygen containing an O^{16}/O^{18} ratio of 180. Since the experimental error was high due to the small size of the samples and the low enrichment, it is proposed to repeat these experiments employing oxygen 20-fold richer in O^{18} than was used in the present experiments.