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CHEMISTRY DIVISION

DECOMPOSITION OF WATER AND AQUEOUS SOLUTIONS

UNDER PILE RADIATION

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CHEMISTRY DIVISION

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UNDER FILE RADIATION

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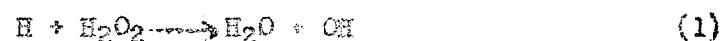


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ABSTRACT

Purified water decomposes under Oak Ridge pile radiation to a slight extent only. The decomposition products, hydrogen and hydrogen peroxide, react with each other under radiation in aqueous solutions to re-form water (back reaction). When the concentration of dissolved products reaches a certain steady-state level, the back reaction rate becomes equal to the decomposition rate and reaction ceases. The steady-state level of hydrogen from purified water in the Oak Ridge pile at 25° C. is about 20 micromoles per liter, corresponding to a hydrogen pressure over the water of only 20 mm of mercury. The presence of impurities markedly increases the steady-state level, and it drifts upwards with time because of slow contamination with impurities from the vessel walls. Some dissolved substances raise the steady-state level much more than others; in HCl and CuSO<sub>4</sub> solutions, hydrogen pressures of hundreds of atmospheres can be obtained, but HgPO<sub>4</sub> and KOH solutions behave much like pure water. The steady-state level is markedly reduced by an increase in the temperature. Addition of a fraction of an atmosphere of hydrogen gas to purified water suppresses the decomposition almost completely; but addition of hydrogen peroxide or oxygen increases the decomposition, so that more hydrogen is obtained from oxygenated water than from initially gas-free water. The results are explained in terms of the behavior of free radicals H and OH formed when radiation splits the water molecules. Radicals formed in high concentration in regions of high ionization density (tracks of proton recoils) frequently react with one another to give H<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> before they can diffuse out into the water. Radicals formed by fast electrons are initially much farther apart and mostly escape

into the bulk of the solution where they may react with solutes. Back reaction is brought about by a radical chain reaction:



Dissolved foreign materials react with radicals, preventing reactions (1) and (2) from occurring until the concentrations of  $\text{H}_2$  and  $\text{H}_2\text{O}_2$  become high; so that the presence of dissolved material raises the steady-state level. Excess peroxide inhibits the back reaction by removing  $\text{OH}$ :



Decomposition of peroxide to oxygen is brought about by (3) followed by

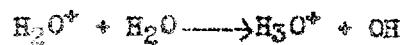
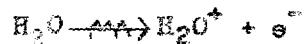


Reaction (5) is apparently catalyzed by dispersed glass particles. The kinetics of the pile-induced reaction between dissolved hydrogen and hydrogen peroxide was studied in some detail and the results interpreted in terms of the above reactions.

## I. INTRODUCTION

The chemical effects of radiation on water and aqueous solutions are complicated. Published data on the subject do not appear to give a consistent picture. The effect of pile radiation on water and various solutions is of technological importance, and the whole subject of radiation effects in aqueous systems is fundamental to a proper understanding of radiobiological mechanisms. We have, therefore, attempted to make a comprehensive basic study of the effects of pile radiation on aqueous systems.

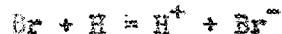
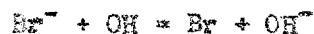
Experiments at the Metallurgical Laboratory<sup>(1)</sup> showed that x-rays or fast electrons decompose water to only a small extent; as soon as the decomposition products, hydrogen and hydrogen peroxide or oxygen reach a level of a few micromoles per liter, a back reaction sets in between the products to re-form water, so that no further changes are seen after a low pressure of gaseous decomposition products has been reached. With alpha rays, on the other hand, the literature<sup>(2)</sup> shows that water decomposition continues without apparent back reaction, at least up to hydrogen pressures of a considerable fraction of an atmosphere. The primary chemical effect of radiation is probably to form the free radicals H and OH according to the mechanism



In heavily ionizing radiation, such as alpha rays or the fast proton recoils formed by the passage of fast neutrons through water, the radicals are formed in high concentration along the track of the particle. In this small zone, the radicals will react with one another to form, to a certain extent, the

molecules  $H_2$  and  $H_2O_2$ . Some of the radicals will be able to escape from the zone and will react with dissolved  $H_2$  and  $H_2O_2$  molecules in the solution to lead to the re-formation of water. When fast electrons are the ionizing agents, the radicals are not so densely distributed and a much larger fraction of them will be able to react with dissolved product molecules before they disappear by reaction with one another. Thus, with heavy particle radiation, a much higher concentration of products in solution will be required before the rate of the back reaction becomes equal to the rate of the forward reaction. Pile radiation is mixed; it contains both gamma rays and the fast neutrons. Consequently, one would predict a steady state lying higher than that for gamma rays alone, but lower than that for alpha rays.

The Metallurgical Laboratory experiments<sup>(3)</sup> showed that the steady-state concentration of products of water irradiated with electrons or X-rays was greatly increased by the addition of small quantities of certain dissolved materials, notably bromide ion and dissolved pyrex glass. Such substances presumably interfere with the radical-induced back reaction by reacting themselves with radicals. Thus with bromide ion, we may assume the reactions



Such reactions remove radicals so that they cannot react with dissolved hydrogen, hydrogen peroxide or oxygen. When sufficient reactive solute is present, the water decomposition will proceed to indefinitely high product pressures. The rate of hydrogen production in such solutions therefore gives a measure of the rate at which the product molecules are formed in the

radiation track. We predict that this rate should be greater the more densely ionizing the radiation. The objectives of the present work were to determine the degree to which water will decompose under pile radiation in the presence and absence of various types of dissolved materials and impurities, to determine the rates at which decomposition and back reaction occur under pile radiation, and to establish the nature and kinetics of the important free radical reactions occurring in the system.

### II. DECOMPOSITION OF PURE WATER UNDER PILE RADIATION

1. Preparation and exposure of silica ampoules - Water was exposed in the vertical water-cooled hole (hole number 12, maintained at 25° C.) of the Oak Ridge pile. The water samples were sealed in vessels made of fused silica tubing. Fused silica was used because it is more inert chemically toward water than most other materials and because it contains no great amount of any elements which become highly radioactive in the pile or act as pile poisons. Most of the ampoules used for pure water were made from 15 mm O.D. tubing, and held about 10 cc; some ampoules were made from 6 mm O.D. tubing and held about 2 cc. The tubes were sealed shut at one end and drawn down to small diameters at the other. After thorough cleaning with sulfuric-nitric acid mixture and rinsing and staking with distilled water, the ampoules were sealed to a vacuum line and flamed to a red heat under vacuum. Degassed water was then distilled into the ampoules from a fused silica container and the ampoules sealed off. In some cases, the ampoules were practically full of water. In other cases they were only partially filled.

Except when otherwise noted, Hole 12 was maintained at 25° C. during the exposures. The water samples were probably about three or four degrees above this temperature, because of the heat resulting from absorption of

radiation in the water.

After exposure for a predetermined time in Hole 12, the ampoules were withdrawn from the hole and allowed to stand for a time to allow the silicon activity to decay to a reasonably low level. The required cooling time varied from an hour to a day, depending on the length of the exposure.

2. Analysis of decomposition products - The exposed ampoule was then placed in a glass tube which was connected to a vacuum line. This tube was evacuated, and the ampoule was broken, either by warming the water in it with a heat lamp so that it expanded and broke the ampoule, by freezing the water so that the ampoule broke, or by breaking the ampoule under vacuum with a mechanical device. After the ampoule was broken, the water was warmed to reflux to assure expulsion of all gas, and the evolved gas passed through a trap maintained at ~100° C. which collected all but traces of water vapor.

The gas was collected in a gas analysis system which consisted of a McLeod gauge connected to a platinum filament and a small liquid nitrogen trap. The gases present were assumed to consist of hydrogen, oxygen and carbon dioxide, with perhaps traces of nitrogen. The pressure of the gas was initially measured in the McLeod gauge. Liquid nitrogen was then placed around the trap, and the reduction in pressure gave a measure of the carbon dioxide content. Considerations of vapor pressure and solubility allowed the conclusion that this component could not be any other substance which might conceivably form in the system, such as ozone, a silicon hydride or a nitrogen oxide. The hydrogen and oxygen were then determined by combustion on the heated platinum filament. Provision was made for the addition of small quantities of hydrogen and oxygen from the outside so that, by further combustion, a complete determination of hydrogen, oxygen and nitrogen in the gas was obtained. The diffusion of gas

from the McLeod gauge to the cold trap and the hot filament occurred rapidly and completely as long as the pressure was kept so low that the mean free path of the gas molecules was of the order of a centimeter. Quantities of gas as small as 1 cubic millimeter (S.P.T.) were analyzed with an accuracy of 1 or 2% in about 20 minutes. Table I shows the results of analyses on synthetic gas mixtures made to test the accuracy of the method. The accuracy of the analysis seems to be good and the chief error is probably the possible incompleteness of removal of dissolved gas from the water sample. A test showed that the first outgassing of a typical sample removed 90% of the dissolved hydrogen, and it may be presumed that gas recovery was at least this good in all the work reported here when the dissolved gas concentration was as high as 300  $\mu$ m/liter.

The volumes of water and gas phase were determined by weighing the ampoule plus water sample, the ampoule full of water and the empty ampoule. For those ampoules which were practically full of water ( $\sim$ 1% gas space in a small capillary) the concentrations of products in micromols/liter were calculated assuming all of the products remained in solution. When a gas phase was present, the concentrations of products in solution were calculated on the basis of known solubilities and the measured amounts of products formed.

The water, after withdrawal of gas for analysis, was removed from the apparatus for calorimetric determination of dissolved hydrogen peroxide. Reagent for the determination was prepared by mixing equal volumes of (a) a solution containing 1 g NaOH, 33 g KI, 0.1 g  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  in 500 ml distilled water; (b) 10 g potassium acid phthalate in 500 ml distilled water. The alkaline iodide solution is stable, but iodide is slowly oxidized by dissolved oxygen at the pH of the mixed reagent, where peroxide reacts rapidly with iodide in the presence of molybdate catalyst. Samples of water ranging in volume from 0.1 to 2 ml, depending on the peroxide concentration, were mixed with 2.5 ml of the reagent

TABLE I  
ANALYSIS OF SYNTHETIC GAS MIXTURES

Total Gas (cc., Std.)	He added %	He found %	O <sub>2</sub> added %	O <sub>2</sub> found %	CO <sub>2</sub> added %	CO <sub>2</sub> found %	Total found %
0.66 × 10 <sup>-2</sup>	100	100					
0.69 × 10 <sup>-2</sup>	83.2	86.0	84.4	83.4	83.4	83.3	83.3
0.89 × 10 <sup>-2</sup>	82.3	80.5	82.3	82.0	82.6	82.0	82.4
1.27 × 10 <sup>-2</sup>	63.2	68.0	63.3	68.9	70.4	70.3	70.3
0.68 × 10 <sup>-2</sup>	97.3	97.6	97.3	97.1	97.8	97.0	97.2
0.77 × 10 <sup>-2</sup>	96.0	96.0	96.0	96.5	96.7	96.0	96.2
0.88 × 10 <sup>-2</sup>	77.2	78.0	78.2	78.2	80.2	80.0	80.2
1.0 × 10 <sup>-2</sup>	84.2	85.0	84.3	85.0	85.7	85.4	85.1
2.02 × 10 <sup>-2</sup>	86.1	86.2	87.6	87.7	87.4	87.0	87.3

in a volumetric flask and distilled water was added to bring the volume to 5 ml. Samples were placed in a 1 cm. absorption cell and the optical densities were determined with a Beckman spectrophotometer at 350 m $\mu$ , the wavelength of maximum absorption for the triiodide ion. The concentration of iroxide in the original sample, in micromoles per liter, is given by  $(D_s - D_b) \times 40.0 \times D_{11n}$ , where  $D_{11n}$  is the ratio of the volume of the final mixture to the volume of the original sample,  $D_b$  is the optical density (log10/l) of the reagent alone diluted with distilled water, and  $D_s$  is the optical density of the sample. In most determinations the sample in one cell was compared with the reagent blank in another cell in the spectrophotometer, giving  $D_s - D_b$  directly. The method was checked using a series of iroxide solutions prepared by diluting a standard iroxide solution analyzed by the analytical group by the ceric titration method. The determination is good to better than 5% at high iroxide concentrations. At low concentrations greater absolute accuracy was obtained by using the same cell for both the reagent blank and the sample, using for comparison each time the intensity with no cell in the optical path of the spectrophotometer. The probable error at low concentrations is believed to be ± 0.2 micromole per liter.

3. Preparation of water - Great efforts were made to purify the water used, in the belief that irreproducibility of results and poor material balances could be ascribed to traces of impurity introduced with the water. The various water preparations used were as follows:

- (a) Ordinary distilled water from the laboratory supply.
- (b) Triply-distilled. Distilled water was redistilled, first from acid, then from alkaline permanganate, in a closed system allowing no contact with the air. This water, like the other preparations, was degassed on the vacuum line in an all-Pyrex "Kupper" -- a reflux device in which water in a bulb is

circulated through a side-tube in such a way as to produce maximum splashing and opportunity for gas to escape from the liquid, while further fractionation is accomplished in a column packed with Pyrex helices. From the burper, the water was distilled under vacuum at about room temperature into the ampoules, which were cooled with ice water.

(c) Cup-treated. The triply-distilled water above was distilled again; the steam passed through a tube packed with CuO and kept at 700° C to oxidize organic matter, then condensed in the burper. After degassing, the water was distilled into a silica flask before the final distillation into the ampoules, to minimize entrainment of dissolved Pyrex into the ampoules.

(d) Nickel-treated. On the advice of J. H. Bennett, the CuO was replaced with strips of pure nickel, the surface of which was purified by oxidation with oxygen at a high temperature, followed by reduction with hydrogen. The steam was passed over the nickel at 1000° C, and was mixed with a little hydrogen to keep the nickel from oxidation. The idea was that nickel should catalyze the reaction of organic impurities with steam to form oxides of carbon.

(e) Old synthetic. To avoid organic and other impurities present in water from natural sources, water was synthesized from hydrogen and oxygen. The gases were taken from tanks; the hydrogen passed through a liquid-air trap, but the oxygen was not purified. The oxygen was in excess; hydrogen was led into the center of an oxygen-filled bulb through a Pt tube and burned at its tip. The water was condensed in a flask open to the air. It was found to contain nitric acid, which presumably arose from NO formed in the flame by oxidation of nitrogen present as an impurity in the oxygen. The water was re-distilled from alkaline permanganate in the air, then poured into the burper, where it was degassed and distilled into the ampoules.

(f) New synthetic. Similar to the above, but process was conducted in a closed system to avoid contact with air. Water vapor from the burner was condensed in a flask which contained solid KOH and KMnO<sub>4</sub>. It was then distilled through a column packed with glass helices into the burper, still in the presence of an atmosphere of oxygen. The burper was then sealed off and evacuated, and the water degassed. A further refinement added here was washing of the ampoules by reflux from the burper. The ampoules had been sealed in series to a manifold; water distilled into the lowest one of the series first, which was then sealed off and the next highest one allowed to fill, and so on. The lowest ampoule in such a string often showed greater gas production under radiation than the others, which was attributed to washing of impurities from the surface of the upper ampoules into the lowest during the filling. The impurities presumably consisted of material vaporized from the silica during sealing. To avoid this, the strings of ampoules were connected to a manifold at both top and bottom, the lower manifold leading back to the burper. After degassing, water was refluxed through the ampoules and back to the burper. The washable impurities were thus carried back into the main body of the water. The ampoule strings were then sealed off at the bottom and the water distilled into them as usual.

(g) Newest synthetic. The above system was refined in several respects. KMnO<sub>4</sub> was eliminated, since KOH was sufficient to hold back the nitrous acid, and traces of Mn might conceivably be entrained through several distillations. Water from the alkali was distilled into the burper, not through one helix-packed column, but through three such columns in succession. That entrainment of KOH was not important was shown by activating the alkali in the pile before putting it in the flask. The solution before distillation showed over 10<sup>5</sup> counts /min/ml; after distillation through one column, no significant counts. To hold

To dissolve Pyrex to a minimum, the entire burner system was made of fused silica, the reflux tower being packed with pieces of silica tubing. To minimize entrainment during the final distillation into the ampoules, the water was distilled from the burner into an auxiliary silica flask and from there into the ampoules.

No essential differences were detected in the behavior of these various kinds of water under irradiation. In later work the water used was mostly laboratory distilled water which had been redistilled first from acid and then from a sodium permanganate in a Pyrex system and finally redistilled at atmospheric pressure in an all-silica system. This water, when air-saturated, had a conductivity of about  $6 \times 10^{-7}$  mhos which is close to the accepted value for pure air-saturated water. Redistillation of this water from the water column in a silica system gave water with a conductivity of about  $2 \times 10^{-7}$  mhos after comparison and calibration with the theoretical value of  $0.6 \times 10^{-7}$  for absolutely pure water containing only  $\text{H}^+$  and  $\text{OH}^-$  ions.

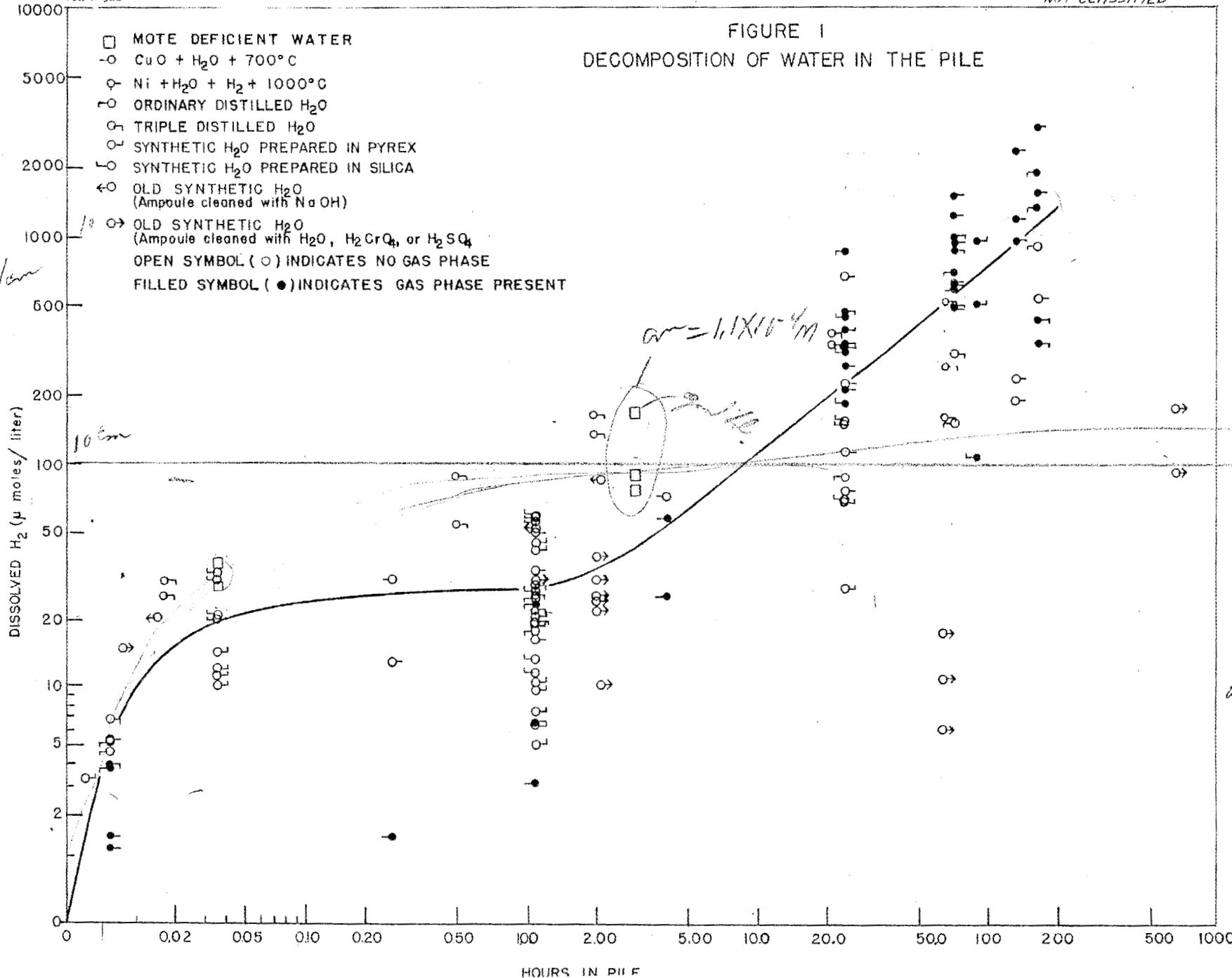
Some water samples were evaporated after irradiation in the pile and the beta activity of the invisible residue was determined by counting. A typical result showed that 5 ml. of water on removal from the pile showed a total beta activity of 250,000 disintegrations per minute. The decay curve broke down into an activity of about 160 minutes, presumably due to silicon, an activity of about 14.6 hours half-life, which might be sodium or potassium and which accounted for 75,000 disintegrations per minute at the time of removal from the pile, plus some longer lived activity. Assuming that the water gave 75,000 dis./minute from Na and 130,000 from Si, a calculation of the total quantities of silicon and sodium present in the water shows that 18 mg. of silicon/liter or  $6 \times 10^{-6}$  M must have been present in the water and 0.14 mg. of sodium/liter or  $1.8 \times 10^{-5}$  M. Those figures seem quite high, since such a

quantity of sodium should give a considerably higher conductivity than observed in our water preparations. It may be that radioactive atoms are dislodged from the wall by recoil when activated, so that the specific activity of the material in the water is considerably higher than normal; this would lead to the results of the above calculation being considerably high.

### III. RESULTS

The concentration of hydrogen produced by the radiation in pure water is plotted in Figure 1 against time of exposure in the pile. Since the solubility of hydrogen in water at the temperatures used (near room temperature) is close to 760  $\mu\text{m}/\text{liter}$ , the concentration of dissolved hydrogen in  $\mu\text{m}/\text{liter}$  is very nearly equal to the pressure of hydrogen over the solution in mm of mercury.

Great irreproducibility is at once evident from this graph. The important factor, however, is that the concentration never becomes very high. For full ampoules, the concentration of dissolved hydrogen within the first few minutes rises to values of the order of 20  $\mu\text{M}$  and remains at this level without great change up to an hour. On exposure of many hours, the concentration tends to drift upwards. Thus, it seems that the water decomposition reaches a steady state within two minutes, but that this steady state tends to drift upwards slowly in the course of time presumably because of contamination of the water by impurities coming out of the vessel wall. For samples with gas phase (ampoules only partly full) the gas formed goes largely into the gas phase, so that the initial rate of rise of concentration of dissolved hydrogen with time is much less. In the course of a day in the pile, however, the steady state is reached also in these ampoules, and the concentration of dissolved gas, as calculated from its solubility, not only reaches, but appears to exceed, the concentrations found in the filled ampoules. The tendency for greater hydrogen concentrations at large gas phases is to be ascribed to the higher  $\text{H}_2\text{O}_2/\text{H}_2$ .



ratios present, and the effect will be discussed further in a later section.

The material balances as shown by the analysis were in most cases very poor. Theoretically, the number of moles of hydrogen formed should be equal to the number of moles of peroxide plus twice the number of moles of oxygen. In Figure 2, the total equivalents of oxidant are plotted against the total equivalents of hydrogen (reductant). Deviations of the points from the 45° line indicate bad material balance. In most cases of poor balance, the hydrogen was in excess. The deviations in many cases were much too large to be explained by errors in the analytical procedure. It seems that either some reducing impurity was present in the water in unexpectedly large amounts, or that the vessel wall enters into the reaction in some way, possibly by the formation of some sort of polysilicic acid complexes.

Carbon dioxide appeared in the products in variable amounts, ranging up to 15 or 20  $\mu\text{M}$ . Usually the CO<sub>2</sub> was present in considerably smaller quantities than the H<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>, but in a few cases of small decomposition, it appeared to be an important product. In the material balances discussed above, CO<sub>2</sub> has been ignored; but including it among the oxygenated products did not on the average improve the material balance. The CO<sub>2</sub> still appeared on irradiation of the most carefully purified synthetic water, and therefore probably does not arise entirely from organic impurities in the water. Perhaps some carbon-containing impurity is present in the fused silica containers, which passes into the water as CO<sub>2</sub> under the action of radiation.

A quantity of interest is the extent to which the oxygenated product appears as oxygen gas or as hydrogen peroxide. The ratio  $\text{H}_2\text{O}_2/(\text{H}_2\text{O}_2 + 2\text{O}_2)$ , which gives the fraction of total oxidant present as peroxide, is plotted in Figure 3 against time. The points are seen to scatter very badly. It is

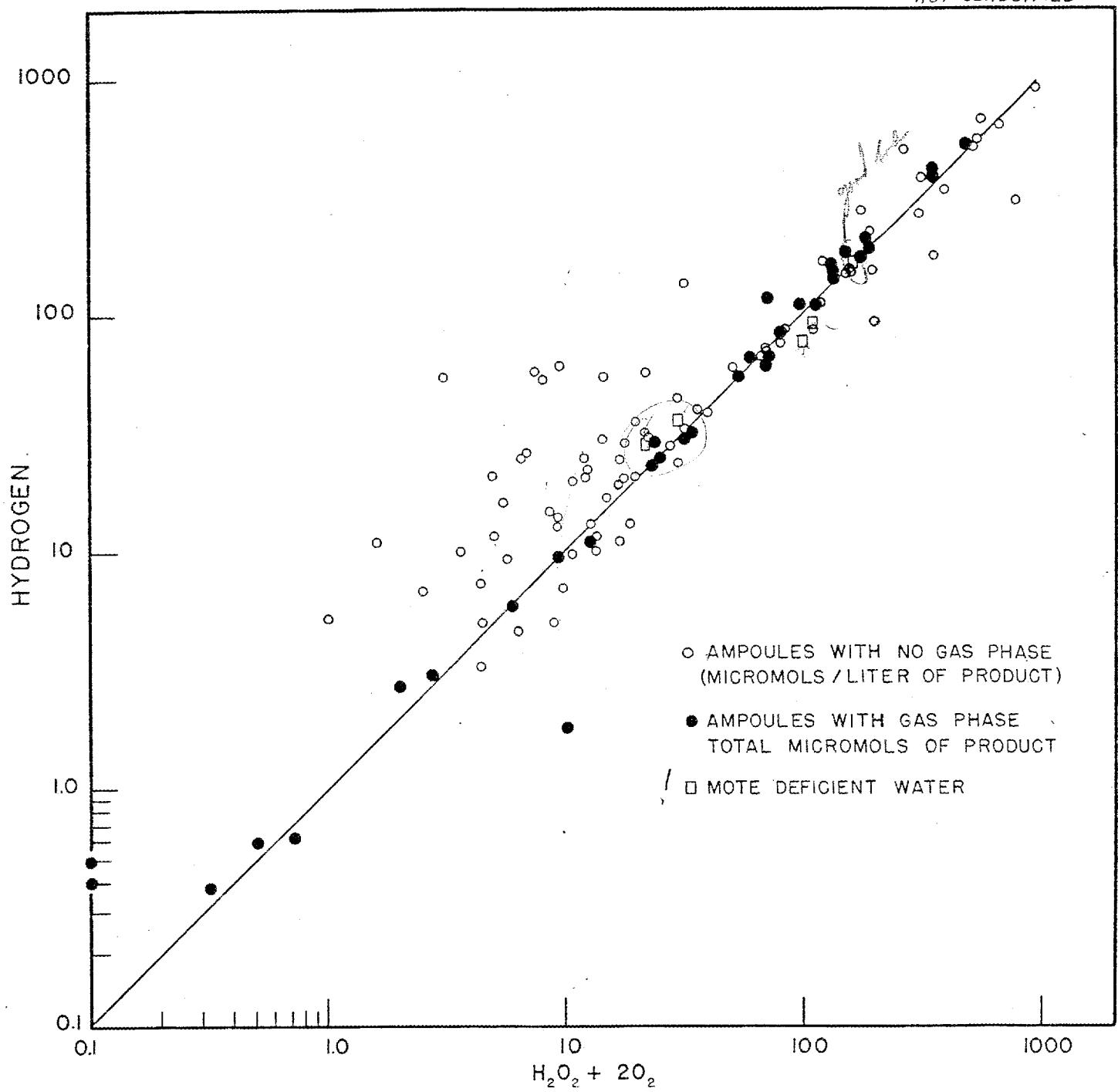
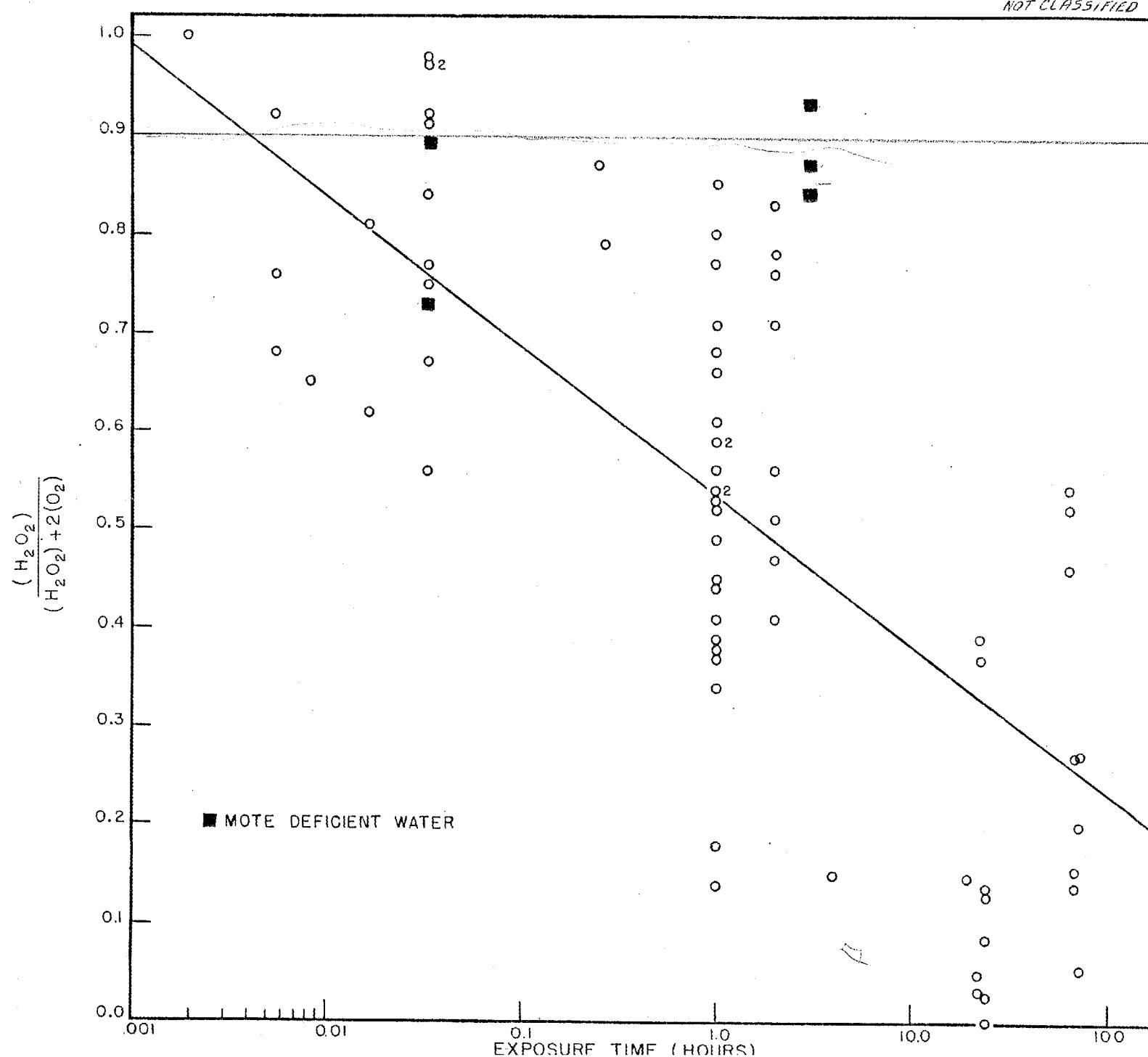


FIG. 2 BALANCE BETWEEN OXIDANT AND REDUCTANT PRODUCED ON IRRADIATING WATER IN THE PILE



clear, however, that at short exposures the oxidant is present mostly in the form of peroxide and that with increasing exposure time the oxygen tends to become more prominent. There is little doubt that the initial product of the reaction is hydrogen peroxide and that oxygen forms by subsequent decomposition of the peroxide. The photochemical decomposition of peroxide is known to be very sensitive to the presence of impurities, especially dissolved or suspended particles of glass. The rate of back reaction of the products will naturally be dependent upon whether the reacting material is oxygen or peroxide, and much of the irreproducibility in the amount of decomposition can be attributed to difference in the fraction of peroxide decomposing to oxygen.

1. "Mote-free" water - Reference to the literature<sup>(4)</sup> on photochemical decomposition of hydrogen peroxide to oxygen in aqueous solutions shows that the determining factor in the quantum yield for the reaction is the number of dispersed particles or motes. It is believed that the radicals formed by photochemical action on the peroxide react on the surface of the motes with the adsorbed peroxide or HO<sub>2</sub> radicals to give enhanced reaction. By special treatment of the container and water to eliminate motes or reduce their number, the quantum yield can be considerably reduced. The same factors might be thought to operate in the decomposition of water under high energy radiation. Samples of water sealed in silica were therefore prepared, following the directions given by investigators of peroxide photolysis for reducing motes to a minimum.

The procedure used was that of Martin<sup>(5)</sup>. Motes are formed by the action of water on a rough glass surface. To make a surface smooth, the glass (fused silica) was heated to the fusion point and cooled in the absence of moisture, since water vapor apparently invades the glass during cooling and causes surface

roughening. Water was then distilled into the ampoule very slowly under vacuum. Some mites are said to be present, nevertheless, and these were removed by pouring the water carefully out of the ampoule back into the distilling bulb and redistilling. This process of distilling and pouring was repeated nine or ten times. Finally the ampoules were sealed off at the small capillary which connected them to the distillation tube. The amount of water in the ampoule was adjusted so that when it warmed up to room temperature no void was left in the ampoule.

The yields of hydrogen, the oxidant-reductant balance and the peroxide-oxygen ratios given by 5 samples of mite-free water are among the results shown in Figures 1, 2 and 3. The peroxide-oxygen ratio was higher in these samples than in most of the other water used, particularly in the case of the three-hour exposures. This is a good indication that with high energy radiation, as well as with ultra-violet light, the decomposition of peroxide to oxygen is hastened by the presence of dispersed glass particles. We believe that the decomposition of peroxide to oxygen is brought about by the reactions



One or both of these reactions occurs more readily on surfaces than in solution. The rate of the back reaction must certainly be affected by the peroxide-oxygen ratio in any solution, since the nature of a reactant is certainly a factor in determining a reaction rate. The irreproducibility of the steady-state levels in water is consequently ascribed to the irreproducibility in the peroxide-oxygen ratio.

## 2. Containers of materials other than silica -

- a) Pyrex - This material is ordinarily not used in the pile since it contains boron, which is a pile poison. We preferred silica also because the Metallurgy

laboratory results with that electrons seemed to indicate that the steady state was very sensitive to the presence of transited types. No attempts were made to correlate with the PMS response. This sample was without any void spaces. In other cases the void spaces took about ten minutes to settle, and caused cracks within samples filled to the same power indefinitely in two hours when placed in the tube. During the testing of the sample caused by the void spaces to settle into a pyramidal shape & which would penetrate to the sample in the test tube. The final test specimen gave results comparable to those obtained in stick like a rod with ordinary compression. After the settling of the voids there should no longer appearance of the solid object of porous type.

The last 1/4" pieces were also placed inside the tube with a thin film of oil by spreading on the specimen from a lamp and flame. Next was distilled water then finally the smaller were pushed and placed in the tube surrounded with 0.020" wire and drawn by aluminum foil to insulate the water while allowing circulation. After being dry heat sterilized, weighed all the contents of the specimen thought to have been a complete absence of hydronium peroxide due to balance between the hydroxyl acting present in considerable measure probably still has not completely lost material to other under the conditions of thermal sterilization.

6. The 1/4" lengths of cellulose were spun forced into cylindrical shapes and the same sealed by fusing with a torch. The tubes were cleaned by sterilizing in autoclave. They were then filled with water and placed in a cellulose container, and the water was contained by pushing sodium through it. After this water dried, the open top of the tube was exposed first with the special clamp and while primed, the top open end was fused with a torch. This procedure was followed for various lengths and sizes to used in the tube. These procedures

were withdrawn by piercing the tube under vacuum with a needle, which was attached to a heavy weight lifted over the ampoule by a magnet and then let fall to pierce the tube. Completeness of removal of dissolved gas through the resulting small hole is somewhat dubious. The tin was activated to some extent in the pile, but after cooling one day could be handled conveniently. Spectroscopic analyses of the tin showed only faint traces of silver, copper, iron, magnesium and lead.

Results of the experiments are shown in Table 2. The results are confusing in that ampoules which contained very little gas space showed no oxygen or hydrogen peroxide, although considerable hydrogen gas was present; but ampoules which contained 14% or more of gas space showed high concentrations of hydrogen peroxide, and oxygen was formed as well as hydrogen. Tin does not seem to be a particularly promising material for experimental work in the radiation chemistry of water.

Table 2. Decomposition of Water Exposed to Clinton Pile  
Radiation in Tin Containers

Exposure Time	Void Space, % ( $\pm 2\%$ )	Product Concentrations, $\mu$ moles/l.			Total Microequivalent	
		H <sub>2</sub>	O <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>	Reductant	Oxidant
2 min.	-	-	0	0	-	-
	-	-	0	0	-	-
3.25 hr.	10	283	223	550	43.6	56.6
	16	-	~0	304	-	-
	16.5 hr.	-	-	413	-	-
16.5 hr.	0	850	0.0	0.0	-	-
	3	250	0.0	0.0	-	-
	20 hr.	-	-	-	-	-
20 hr.	0	296	0.0	0.0	-	-
	14	450	250	880	121	106
	31	248	170	660	190	178

d) Zirconium - Since zirconium is a relatively newly available metal of interesting properties, experiments were done to see if the presence of this metal had any great effect on the decomposition of water. Two fused silica ampoules of about 10 ml. capacity, each containing about 15 cm<sup>2</sup> of 28-mil zirconium sheet were completely filled with pure outgassed water. The ampoules were irradiated for one hour, opened, and the contents withdrawn for analysis; the same ampoules were then refilled and re-exposed. Results are shown in Table 3. The results of the second fillings may indicate uptake of gas by irradiated zirconium.

Table 3. Decomposition of water under one-hour Oak Ridge Pile Radiation in fused silica containers containing sheet zirconium.

Ampoule	Filling	Product Concentrations, micromoles/liter			
		H <sub>2</sub>	O <sub>2</sub>	CO <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>
1	1	287	84	8	71
	2	22	0	11	0
	3	125	15	8	76
2	1	71	1.6	0.3	21
	2	17	1.1	12	0
	3	64	8	0.7	26

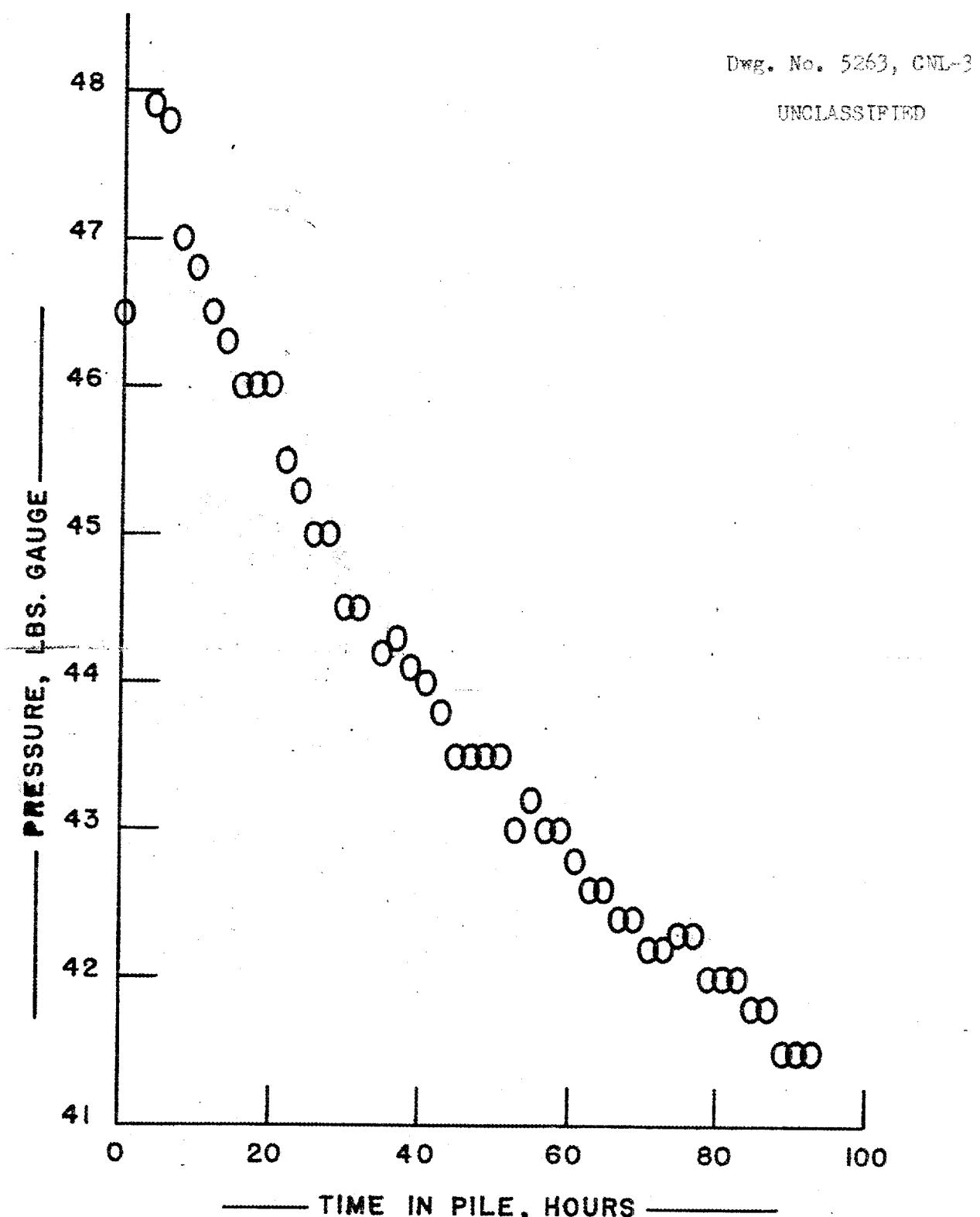
e) Aluminum - Previous reports showed that pieces of aluminum appeared to increase the amount of decomposition obtainable by pile radiation from water sealed in silica. Because of the utility of aluminum as a material for containers for pile irradiation, an attempt was made to find out the gas pressure obtainable in the Oak Ridge Pile by decomposition of water placed in a vessel made entirely of aluminum. We were assisted by Mr. S. Untermeyer in the preparation of this experiment. A 2S aluminum can was fabricated from drawn

tubing; the end plugs were heliarc welded. The surface was seasoned by filling the can with distilled water and bringing to a boil several times. The can was then emptied, and refilled with triply distilled water. After filling, a 15-foot length of 2-mm aluminum capillary tubing (28) was heliarc welded to the top of the can and a pressure gauge and a long mercury manometer were fitted to the free end of the capillary. The system contained 450 cc of water and a total gas volume (not including the manometer) of 116 cc. The system was pressure-tested with 150 pounds gauge of nitrogen. No leaks were shown after standing overnight, so the can was lowered to the maximum flux position of the vertical water-cooled hole #12 in the pile.

The gauge and manometer readings were followed with time in the hope that the pressure would level off to a steady value. The pressure actually rose for several days with little decrease in rate. Part of this time the hole was maintained at 8° C. Later the temperature was increased to 12° C. A pile shutdown occurred, and it was found that the pressure continued to rise as fast when the pile was off as when the pile was running. Thus the pressure rise was not due to radiation decomposition of the water at all, but rather to reaction of the water with aluminum to form hydrogen gas.

The can was withdrawn from the pile, and the pressure was found to remain steady when the can was kept in the air at about 20° C. To reduce the aluminum still further, the can was then placed several days in a water bath kept at 80° C. The pressure kept rising during this treatment. The temperature of the bath was then lowered to 30° C. and no significant further pressure change occurred in the course of several days. The metal was then regarded as having been completely passivated with respect to reaction with water at room temperature.

The can was then replaced in the pile, the hole being maintained at 80° C. The subsequent pressure readings are shown in Figure 4. It is seen that after



**FIGURE 4. Gas Pressure Over Water In Aluminum Can Placed In Clinton Pile.**

an initial pressure rise due to heating of the water by radiation, the pressure steadily dropped. The pile was shut down after 96 hours and the can was re-opened although the pressure was still dropping. A sample of the gas withdrawn for analysis was found to contain 75% hydrogen and 25% oxygen. The balance was presumably nitrogen. (It may be seen that the amount of nitrogen remaining was not as much as expected from the fact that the gas volume originally contained 1 atmosphere of nitrogen. Probably the nitrogen was lost when the canister was cut off from the rest of the system, which was done when the pressure reached a value of 38 pounds gauge since the manometer had at that point reached its limit.) The water in the can was tested for hydrogen peroxide and the concentration found to be less than  $10^{-3}$  M. The drop in pressure during the irradiation must be attributed to back reaction between hydrogen and oxygen dissolved in the water, since the rate of this reaction was far too rapid to be attributed to a reaction occurring in the gas phase.

Thus it is shown that in an aluminum vessel the steady-state pressure of oxygen obtainable by radiative decomposition of water at  $\sim 80^\circ C$ , in the Oak Ridge pile is less than 8 pounds of oxygen, provided a large excess of hydrogen gas is present. It is evident that the oxygen was generated by radiative decomposition of the water at a time when the excess hydrogen had consumed less; the subsequent transmutation of the can outside the pile resulted in the generation of more hydrogen, and when the can was re-opened in the pile, this excess hydrogenated the water decomposition and reacted with oxygen to re-form water causing a pressure decrease.

The experiment demonstrated that Al is not a very powerful inhibitor for the back reaction. The fact that it does inhibit the back reaction somewhat was demonstrated by some other experiments in which pieces of Al were mixed with water

iodide ampoules of cellophane and irradiated in the pile. Three aluminum rods, 3/16" in diameter and about 2" long, were sealed with a few ml. of water in each ampoule. To prevent corrosion, some of the pieces were anodized; others were boiled in distilled water. With no radiation the hydrogen yield was 3  $\mu\text{M}$  for the anodized samples and 40 to 60  $\mu\text{M}$  for the boiled samples. On irradiation, the water gave more hydrogen than in the absence of aluminum; thus in two hours in the pile, 697 and 547  $\mu\text{M}$  hydrogen was formed in the presence of anodized aluminum, and 1160 and 1220  $\mu\text{M}$  with boiled aluminum, together with appreciable amounts of oxygen and peroxide.

### 3. Pressure indicating ampoules

Results obtained with different ampoules were so erratic that it became obviously desirable to measure the pressure of gas in an ampoule without opening, if so that the development of gas could be followed as a function of exposure time in a single ampoule. This was accomplished by deviating an arrangement for determining the boiling point of the water in the ampoule. The method is illustrated diagrammatically in Figure 5. The main part of the fused silica ampoule is drawn out into a capillary, a few cm. long, terminating in a small bulb into which is ring-sealed a further length of 1-mm. bore capillary, with the lower end ground to a tip. The ampoule was generally about half-filled with water; the method of filling was the same as for the regular ampoules. To measure the boiling point, the ampoule is placed vertically, with the capillary end down, immersed in a heated bath. The main upper part is immersed in an ice-bath. The lower capillary is heated to expel the gas from it. Bubbles of gas emerge from the capillary tip and pass through to the upper chamber. When bubbling stops, the end capillary should ideally contain water vapor only. The lower bath is then slowly cooled, until the temperature in the lower bath drops to the boiling point  $T_b$  of the

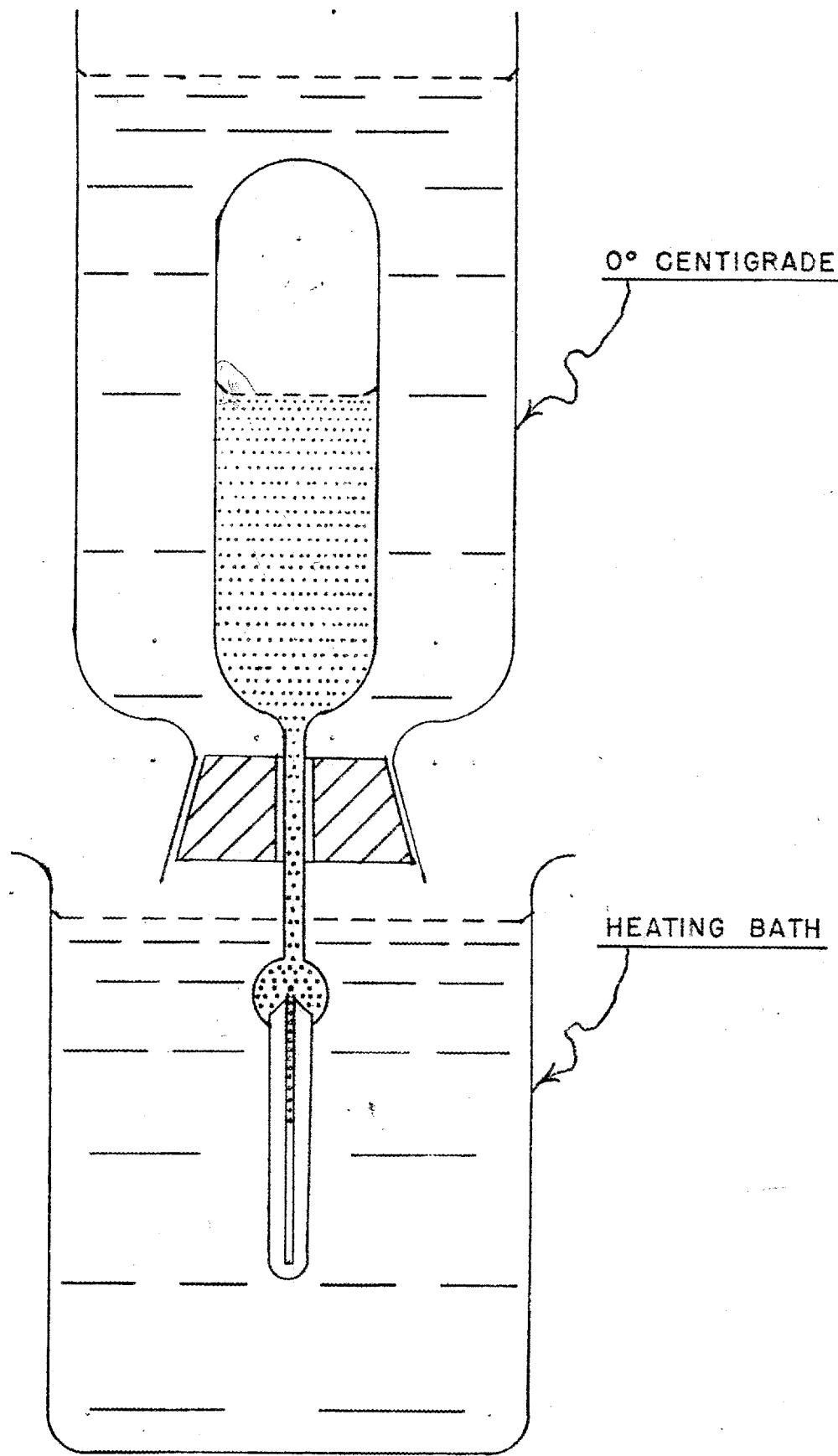


FIGURE 5, Determination of Pressure in Pressure-indicating Ampoule

water under the ambient pressure, the vapor should suddenly condense and water rush in to fill the capillary. The pressure of gas  $P_0$  in the main part of the ampoule would then be the vapor pressure of water at  $T_b$ ,  $P_{vb}$ , less the head of water  $h$ , less the vapor pressure of water at the ice point,  $P_{vo}$ . (The head  $h$  equals the actual distance between the upper and lower water menisci, plus 3 cm. to take account of the capillary rise effect.) In practice, it is impossible to get rid of all the gas in the capillary, so that the water, instead of coming down suddenly into the capillary, comes down gradually over a range of 1-2° in the bath temperatures. The best procedure then is to note the temperature  $T_1$  at which the volume of vapor phase remaining in the capillary is reduced to some value  $V_1$ , and the lower temperature  $T_2$  at which it reaches some smaller value  $V_2$ , which is conveniently taken as one-half of  $V_1$ . Then if  $P_{vt1}$  and  $P_{vt2}$  are the vapor pressures of water at  $T_1$  and  $T_2$ ,  $P_{g1}$  as the unknown partial pressure of permanent gas in the capillary when the volume is  $V_1$ , and  $P_1$  and  $P_2$  are the total pressures in the capillary when the volumes are  $V_1$  and  $V_2$ , we have, neglecting the Charles' Law, contraction of the permanent gas in the capillary:

$$P_1 = P_0 + h + P_{vo} = P_{g1} + P_{vt1}$$

$$P_2 = P_0 + h + P_{vo} = P_{g1}(V_1/V_2) + P_{vt2}$$

Since the change in  $h$  is negligible, we equate  $P_1$  and  $P_2$ . If  $V_1/V_2 = r$ , we have  $P_{g1} = P_{vt1} - P_{vt2}$ , and finally by substitution:

$$P_0 = RP_{vt1} - P_{vt2} - h - P_{vo}$$

Successive pressure determinations are reproducible to about  $\pm 2\%$ .

#### 4. Rater decomposition in pressure-indicating ampoules; effect of type of radiation on the steady state

A number of these ampoules were exposed in the pile at about 25° C., withdrawing at intervals for pressure measurement. The results are shown in

Figure 6. The rate of gas generation is initially about the same for the different ampoules, but sooner or later decreases and finally becomes zero, (steady state). The final pressure attained varied for the different ampoules from 51 to 147 cm. The corresponding concentrations of  $H_2$  dissolved in the water are of the order of a few hundred  $\mu\text{M}$ . These results confirm the original idea that a steady state for decomposition of water will be attained.

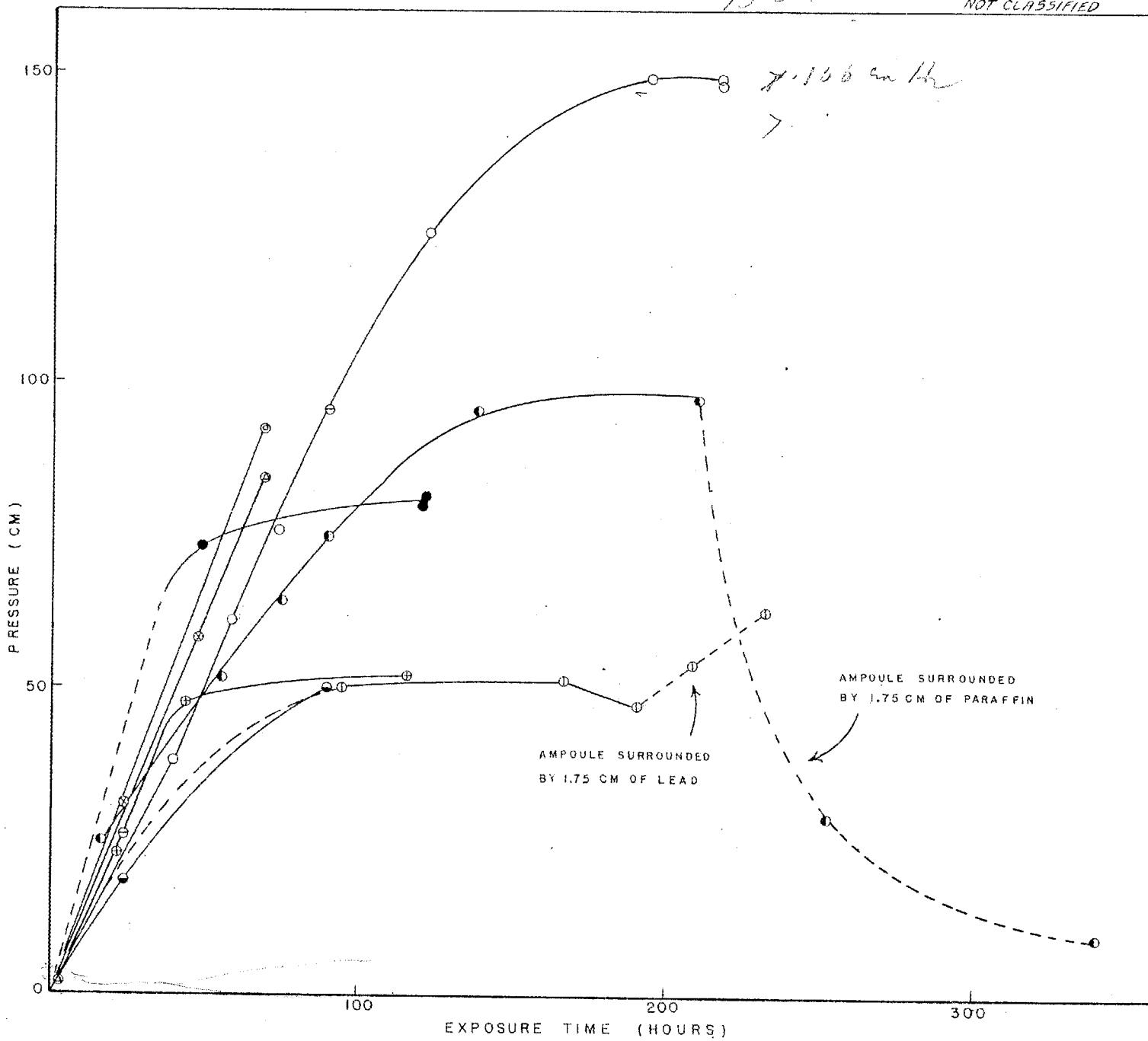
Taking these data, together with those obtained with full ampoules, we get the following picture: In a full ampoule, a steady state is attained within a few minutes. The steady-state level of decomposition gradually drifts upward, however, because of aging of the ampoule which presumably introduces dispersion in the water of material from the wall. In a half-filled ampoule, attainment of the steady-state concentration is necessarily much slower, and the aging process occurs concomitantly with the initial gas evolution, so that a smooth pressure-time curve results. After a few days, however, the aging process appears to reach an end, so that the pressure attains a true steady value. At this point, the dispersion of silica in the water may be balanced by reprecipitation in the wall. Different ampoules give different steady states because the nature of the foreign particles produced varies with different samples of silica tubing. It is very doubtful that the steady-state pressure in these ampoules would remain indefinitely constant. Further aging, would probably occur if the exposures were continued for many weeks.

We were able with these ampoules to confirm the theory that the steady state should be higher the greater the proportion of heavy-particle radiation impinging on the sample - i.e., the greater the average density of radicles at the time of their formation. An ampoule was surrounded with  $11/16"$  of lead. This cuts out much of the  $\gamma$ -rays absorbed by the sample, while reducing very little the fast neutron flux in the water. The steady-state level of gas should, therefore, be increased. This actually happened; the pressure, which had been essentially constant for 95 hours without lead at 48-51 cm., rose in a

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further 44 hours' exposure with lead to 61 cm. Another ampoule, which had leveled off at 25-26 cm., was put back surrounded with 11/16" of paraffin. This reduces the fast neutron flux much more than it reduces the  $\gamma$ -ray flux. The pressure, as may be seen in Figure 6, dropped precipitately, eventually reaching 10 cm. The initial rate of pressure drop when the paraffin was put on was actually greater than the initial rate of pressure rise obtained with fresh samples. This last observation strongly tends to confirm the idea that the back-reaction possesses a chain character.

#### 3. Effect of temperature on the steady state -

To determine the effect of temperature on the steady-state level of pressure in water decomposition, a small furnace was placed in Hale 12. Temperature of the furnaces, measured by a thermocouple connected to a Brown recording controller, was maintained within 1° of any desired value. Water was irradiated in the furnace in pressure-indicating ampoules. The ampoule was kept at one temperature until a steady value of the pressure was reached, as shown by successive pressure readings giving little change; then the temperature was increased and held at the new value until a new steady-state pressure was attained.

The pressure history of the ampoules is shown in Figure 7. Ampoule "A" had been irradiated above the furnace at about 36° C., and had attained a pressure of about six atmospheres. On being placed in the furnace at 110° C., the pressure dropped to about 6 cm. and remained constant, except for a continual rise of about 0.05 cm. per day which was presumably due to aging of the walls. Ampoule "B", introduced later than "A", attained a steady state at 1.6 cm. When the temperature was increased to 150° C., the pressure in "A" dropped to 4 cm. and in "B" to 2.0 cm. Then the temperature was dropped to 42° and the pressure rose markedly, to 31.6 cm. in "A" and 19 cm. in "B".

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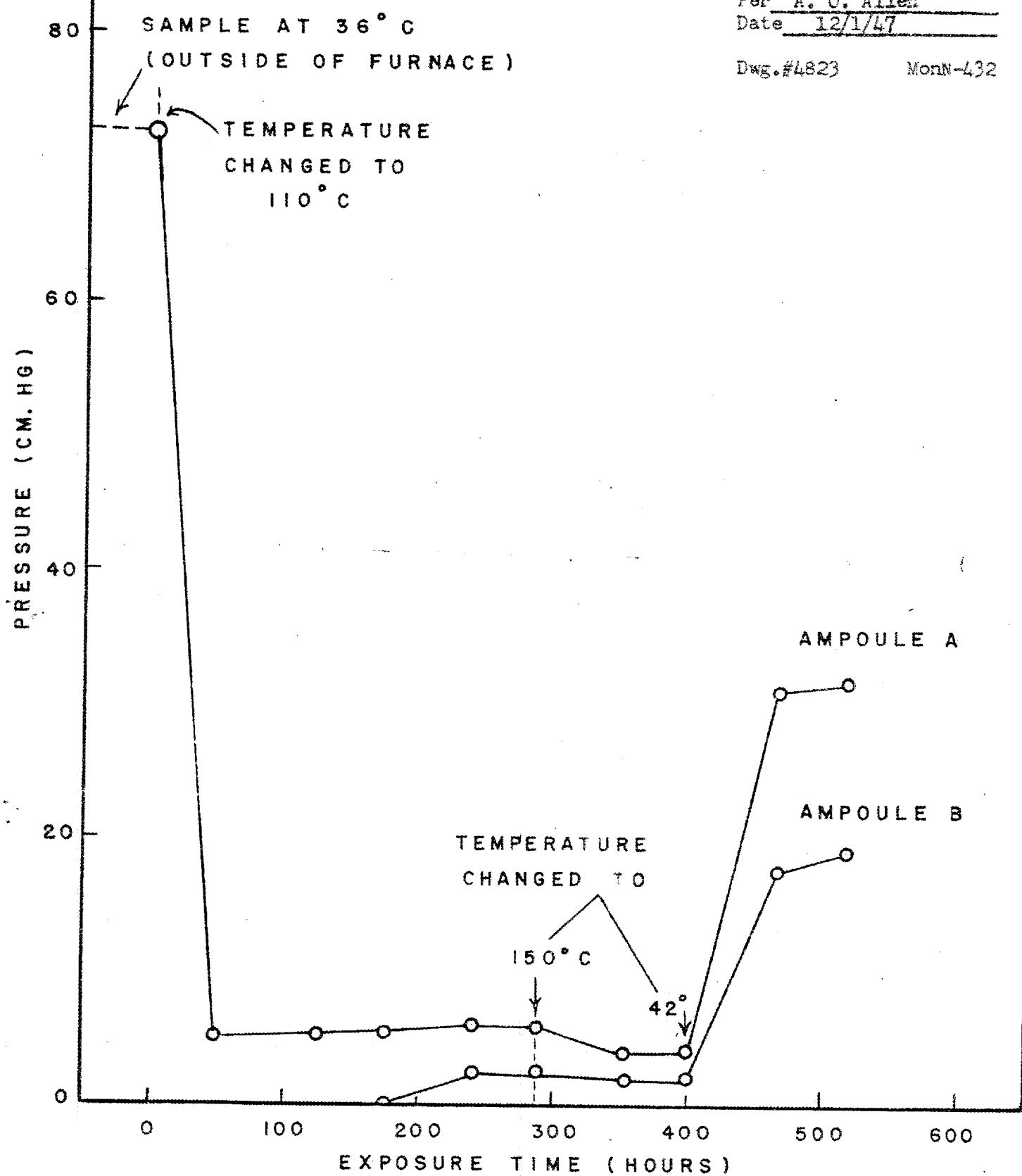


FIGURE 7. EFFECT OF TEMPERATURE ON WATER DECOMPOSITION BY PILE RADIATION

Although the pressures attained in the two ampoules are different as usual, owing to adventitious impurities, the temperature effect on the two was similar. Thus high temperature promotes the back reaction and reduces water decomposition by radiation. The result is of interest in connection with proposed use of high-pressure high-temperature water - moderated reactors for power production.

An attempt was made to verify the temperature effect by exposing sealed ampoules, full of water, for various times at different temperatures, then determining the amount of decomposition by analysis. The results were inconclusive, because of the usual irreproducibility.

#### 6. Possibility of back reaction in the gas phase -

We have assumed throughout that the back reaction which results in cessation of water decomposition under radiation occurs between the products dissolved in the liquid phase. This seems reasonable because the amount of energy absorbed in any phase is proportional to the mass of material present, which is of course very much greater in the liquid phase. If equal volumes of water and electrolytic gas are present, as in the experiments with the pressure-indicating ampoules, the energy absorption in the two phases at 1 atm. pressure will be in the ratio of 18/22,400. According to Lind<sup>(6)</sup> the ion pair yield for the combination of hydrogen and oxygen in the gas phase is about 5. Calorimetric measurements<sup>(8)</sup> show that a gram of water (or electrolytic gas) in Holes 12 absorbs energy at the rate of about  $2 \times 10^{18}$  ev/minute, corresponding to the formation of about  $2 \times 10^{18}/35$  ion pairs per minute. The resulting rate of pressure drop due to this gas phase reaction is readily calculated from the above assumptions to be about 0.00% per hour, or 0.4 mm/hr. at 1 atm. pressure. The pressure-indicating ampoules showed initial

pressure rise rates of the order of 10 mm/hr., and when the temperature was increased from 36° to 110°, the pressure fell at the rate of about 14 mm/hr. The back reaction rate in the gas phase for the case of equal volumes is therefore believed to be only a very few percent of the back reaction rate in the liquid phase; in full ampoules, of course, no gas phase was present and all back reaction must occur in the liquid.

Experimental test of the rate of reaction between hydrogen and oxygen gas in the pile was, however, desirable since one could not be absolutely sure that the ion pair yield in the pile is of the same order as that found for alpha rays. Ampoules, connected to a manifold by narrow capillaries, were filled with electrolytic H<sub>2</sub>-O<sub>2</sub> mixture, the capillaries were plugged with ice by freezing a small drop of water in each one, the manifold flushed with air, and the ampoules sealed off above the ice plug. The amount of water in each ampoule was so small that it completely vaporized at room temperature. Unfortunately, exact results were not obtained, since the initial pressure in any series of ampoules was not exactly the same (probably because the ice plugs were not quite tight). Of six ampoules, exposed in the pile for 20 or 56 hours at 140° or 150° C., five showed no significant drop in pressure; the sixth contained no gas, probably because of an accidental explosion. It may be fairly concluded that reaction in the gas phase is not an important factor in fixing the steady-state level in water decomposition.

#### IV. DECOMPOSITION OF WATER IN AQUEOUS SOLUTIONS UNDER

##### FILE RADIATION

1. Experimental method - Solutions made up using triply distilled water were placed in a fused silica bulb connected to a side arm to which the ampoules were sealed. The bulb was sealed on to the vacuum line and the solution was degassed. The bulb was then sealed off from the line under vacuum, the solution poured into the ampoules and the ampoules then sealed off individually.

All experiments on solutions here reported were made with full ampoules containing essentially no gas phase.

3. Results from various solutions - Solutions of KBr, KI, CuSO<sub>4</sub>, KCl, RCl, KOH, H<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub> and HgPO<sub>4</sub> at various concentrations were exposed for different lengths of time in the pile. Resulting yields of hydrogen gas are shown in Figure 8. It is seen that in many cases, hydrogen concentrations were obtained far exceeding anything found with pure water. In general, the pressure increases with time, then usually levels off to some steady-state value. With the more concentrated chloride solutions and with copper sulfate, the dissolved hydrogen pressure did not level off, even when values corresponding to hydrogen pressures of over 100 atmospheres were attained. The initial rate, however, appeared to be the same in all cases. This is shown in Table 4, which gives the hydrogen yields obtained in 1-minute exposures of the various solutions. The value is always about 27 micromoles/liter within experimental error, except for a few lower values obtained with pure water and solutions that gave low steady-state values; in these cases, the back reaction was apparently already important in the first minute.

These results are readily explained in terms of our picture of the forward reaction, occurring in the densely ionized charged particle tracks, probably independently of the back reaction which comes about through the agency of free radicals escaping from the tracks. Those solutes which produce very high steady states react with radicals, and thereby prevent the radicals from reacting with dissolved hydrogen and hydrogen-peroxide, so that the back reaction is inhibited. The forward reaction proceeds and the observed rate is that of the forward reaction until the dissolved hydrogen and peroxide reach a high enough concentration to compete with the dissolved materials for reaction with the radicals. The observed rate then drops. This falling off occurs at a higher concentration of hydrogen the higher the concentration of any given dissolved material. The relative effectiveness of

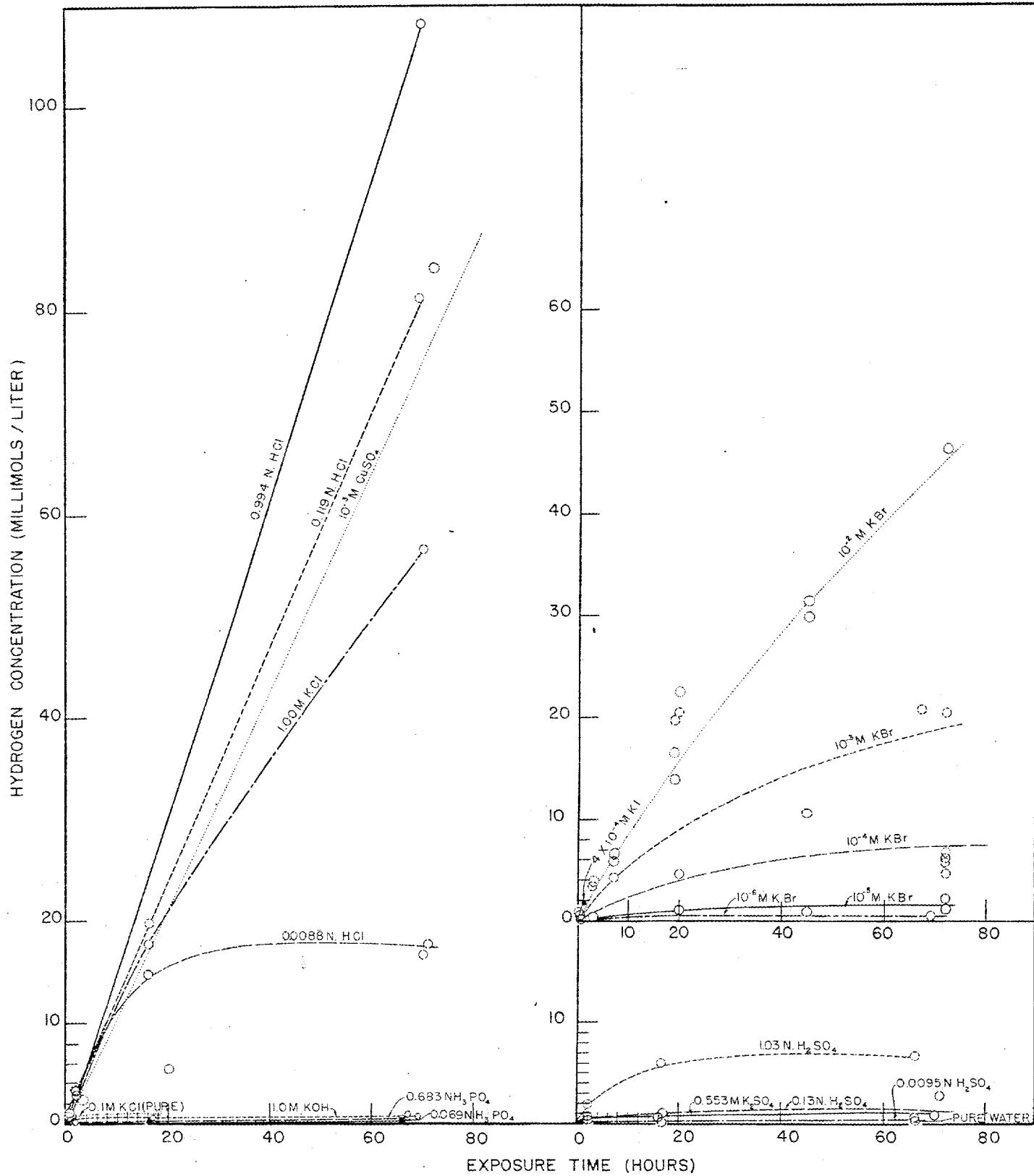


FIG. 8 EFFECT OF SOLUTES ON WATER DECOMPOSITION IN THE PILE

TABLE 4  
YIELDS OBTAINED IN VARIOUS SOLUTIONS IN 1 MINUTE PILE  
EXPOSURES

Solution	Product Concentrations ( $\mu$ moles/liter)		
	H <sub>2</sub>	O <sub>2</sub>	H <sub>2</sub> O <sub>2</sub>
1.0 N H <sub>2</sub> SO <sub>4</sub>	33.7	0.65	52
0.13 N H <sub>2</sub> SO <sub>4</sub>	23.4	0.0	24
0.0095 N H <sub>2</sub> SO <sub>4</sub>	20.8	0.8	20
0.683 N H <sub>3</sub> PO <sub>4</sub>	28.3	0.0	30
0.069 N H <sub>3</sub> PO <sub>4</sub>	25.8	0.0	12
0.994 N HCl	26.9	7.1	70
0.119 N HCl	29.7	0.7	28
0.0088 N HCl	29.0	5.4	5
1.0 M KCl	31.8	6.8	10
10 <sup>-2</sup> M KBr	24.7	8.1	1.2
10 <sup>-3</sup> M KBr	23.8	3.8	1.0
0.5 M K <sub>2</sub> SO <sub>4</sub>	20.3	0.9	8
10 <sup>-3</sup> M CuSO <sub>4</sub>	27.5	3.2	25.2
H <sub>2</sub> O	17.1	0.5	1.6
	30.8	0.0	0.0
	26.2	0.65	5.6

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different materials in raising the steady state is a measure of the specific reaction rates of these ions with the radicals. Evidently bromide, iodide and copper ions react most rapidly with radicals, hydrochloric acid somewhat less rapidly, sulfuric acid still less rapidly, while phosphoric acid and hydronium ions react little or not at all with the radicals. Reproducibility in these experiments was fairly good except for the more dilute solutions. With the more concentrated solutions the effect of the impurities was apparently swamped by that of the dissolved materials. With most of the solutions, the material balances were reasonably good. A few cases of poor material balance occurred, especially with sulfate solutions, suggesting that some oxidation or reduction of the solute may have occurred. The peroxide concentrations were very high in the case of sulfuric acid, suggesting that a persulfuric acid may have formed which is more stable to radiation than hydrogen peroxide. A complete elucidation of what occurs on irradiation of these solutions would require a more nearly complete analysis of the dissolved materials.

3. Purified chloride solutions at various pH - It was suspected that the high hydrogen concentrations shown for irradiated KCl in Figure 8 might have been due to a bromide impurity in the chloride used. Some potassium chloride was specially purified from bromide ion by repeated chlorination and recrystallization. The bromide content was determined by activation analysis. The solid potassium chloride was exposed in the pile. The irradiated salt was dissolved in water and active bromine separated by addition of carrier KBr and excess  $\text{KBrO}_3$ , followed by extraction into carbon tetrachloride. The bromine was then reduced to bromide using  $\text{NaBRO}_3$  with silver nitrate, and the activity was counted in the usual way. To obtain an absolute calibration of the method, other samples of KCl were exposed to which known amounts of KBr were added. The determinations indicated that the molar ratio of  $\text{Br}^-$  to  $\text{Cl}^-$  in the original salt was  $7.5 \times 10^{-7} \pm 30\%$ .

Solutions of the purified chlorite of the desorption with purified hydrochloric acid were drawn into ampoules and were then sealed and kept at 40° until the solution was warmed up to room temperature. On the desorption of the chlorite the same time, a 10% solution of purified 7.5% hydrochloric acid had been added to the solution. Hydrochloric acid was added in excess. However, about one-half mole of hydrochloric acid was added due to the effect of precipitation from the reaction desorption of water which remained in the glass.

A series of solutions were made up from two of the chlorites, all of which were chloride free, but having various values of their hydrogen ion concentrations. The solutions will be used to determine the rate of reaction. Evidence of this reaction will be shown in the form of the ability of the reaction to continue indefinitely, the peak reaction average rate. In these experiments the same active substance, water and salt in the same amounts, are used in each reaction.

In the hydrochloric solutions, the reaction shows that there are three parallel paths for  $\text{Cl}^- + \text{H}^+ = \text{HCl}$ , which is known to be dissociation. These different parallel reactions between chlorine and its chloride, however, result in undissociated and dissociating ions with little release. In this situation it follows, we may formulate the reaction:



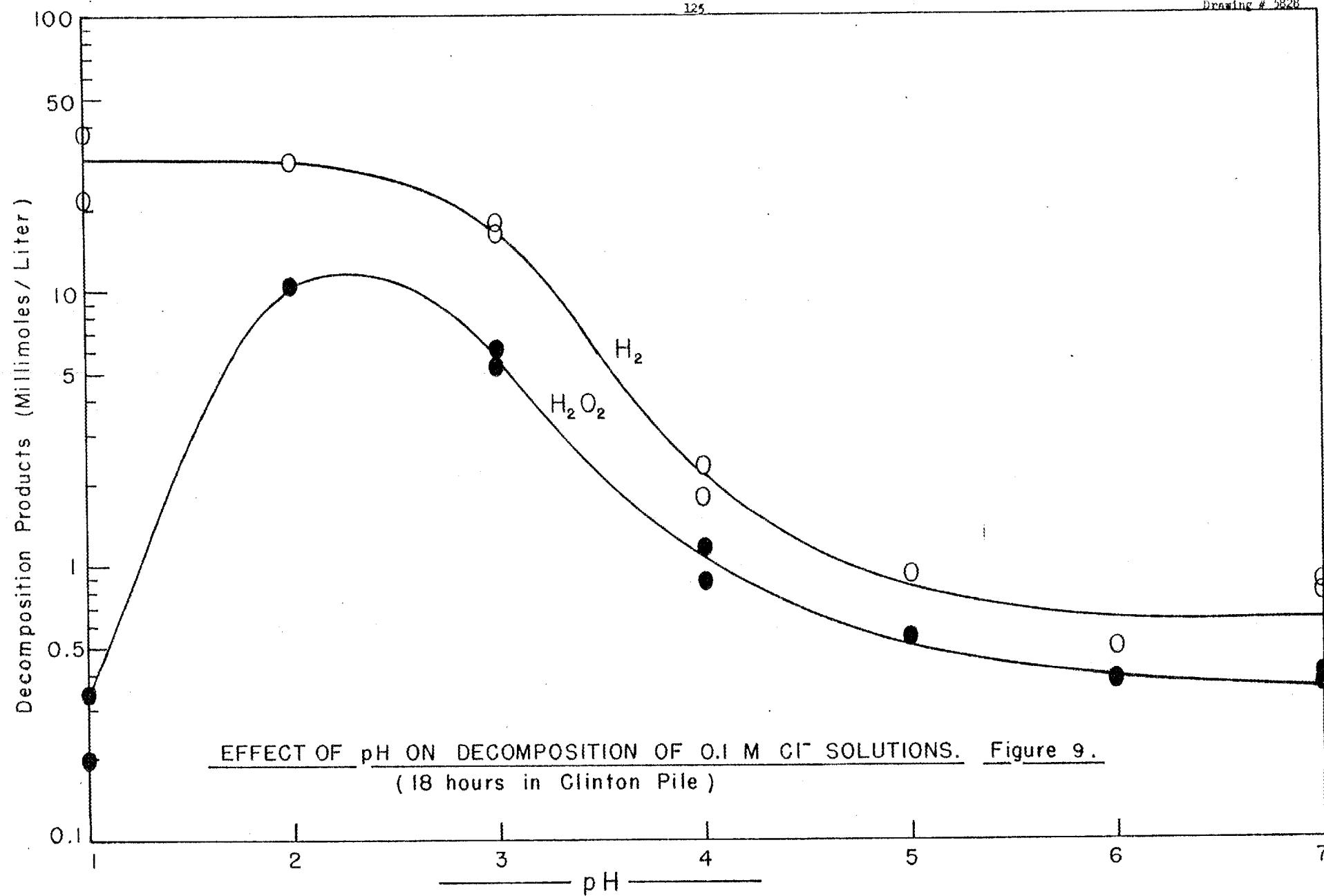
The reaction is favorable when the aqueous acidic solution contains dissolved salts or the products of the dissociation of the hydrochloric acid solution.

A series of 200-ml. solutions having various concentrations of the two solutions were successively made up. The original dissolved salts in which the chloride and hydrochloric acid concentrations were different, was taken up first in this manner. These salt solutions were stored in the tube for 12 hours, which

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was believed to be long enough to reach the steady state in all cases. Results are shown in Figure 10. It will be seen that, as expected, for a given chloride ion concentration, the amount of water decomposition increases with increasing hydrogen ion concentration, and for a given hydrogen ion concentration, the decomposition increases with chloride ion concentration. However, for solutions having different chloride ion concentrations but the same value of the product of hydrogen and chloride ion concentrations, the amount of water decomposition was not always exactly the same but appeared to vary systematically with chloride ion concentrations, especially at the lowest ion product values. The indication is that the trimolecular reaction written above may play an important role but does not tell the whole story.

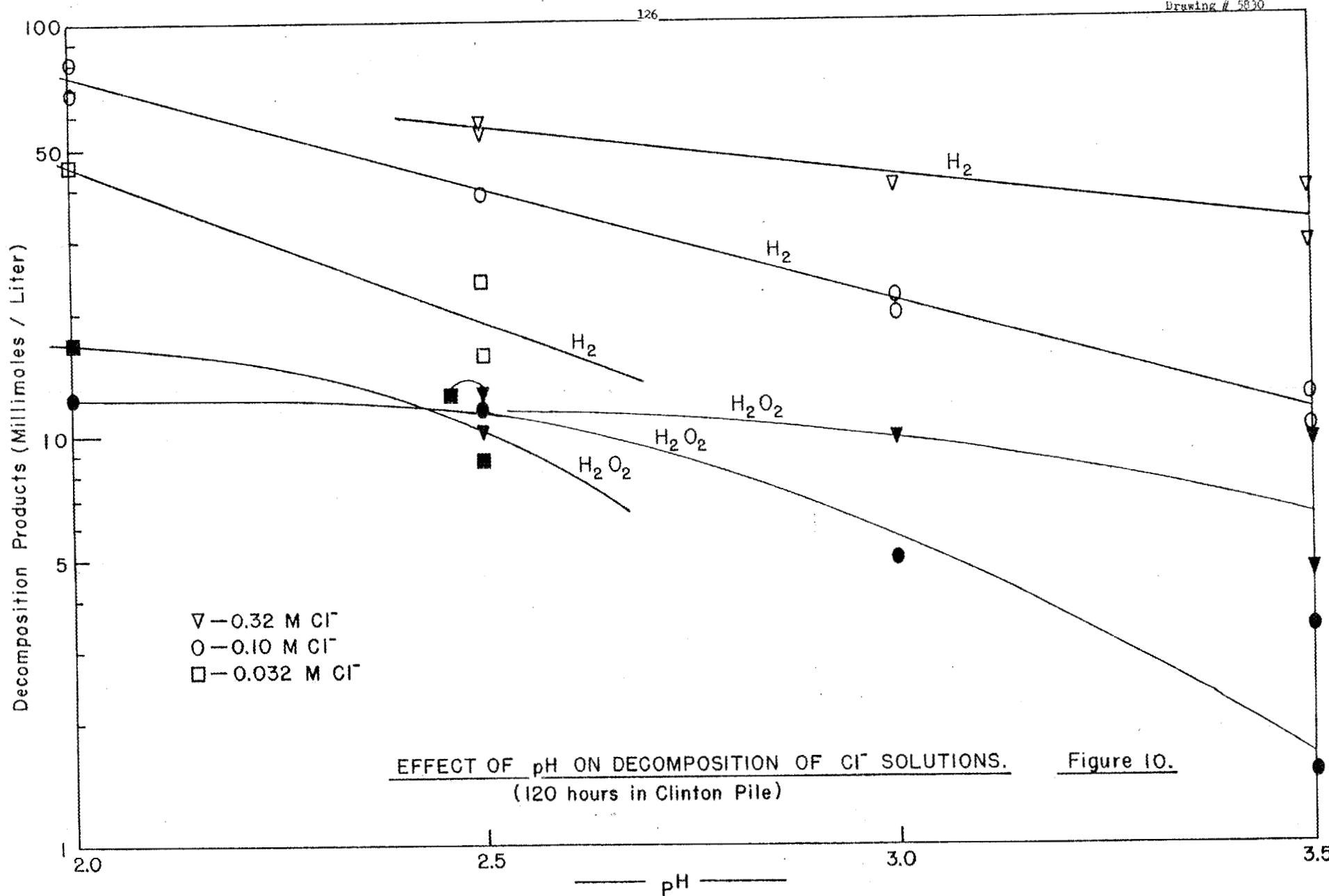
#### V. THE REACTION BETWEEN DISSOLVED HYDROGEN AND HYDROGEN PEROXIDE UNDER FILE RADIATION

Since the back reaction between dissolved hydrogen and hydrogen peroxide plays such an important part in water decomposition, it was obviously desirable to study the rate of this reaction directly under various conditions. The kinetics of this reaction should also give as more detailed insight into the mechanism of the series of radical reactions occurring.

The water was triply distilled in all-silica apparatus. Hydrogen peroxide (Baker and Adamson, reagent grade, 30%) was vacuum distilled in silica apparatus before use. The silica ampoules used were sealed to a silica manifold connected to a silica bulb in which the water or peroxide solution to be used was placed. Hydrogen freed of higher-boiling impurities by passage through a liquid-air trap was bubbled through the solution in the bulb until air was expelled and the solution saturated with the gas at atmospheric pressure. The whole apparatus was then inverted, allowing the gas-saturated solution to flow into the ampoules, which were then sealed off.

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Drawing # 5830



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Solutions were made up in which the hydrogen was in excess of the peroxide and others in which the peroxide was in excess. The most interesting results were obtained from solutions in which hydrogen was in excess. Figure 11 shows the change of peroxide concentration with increasing exposure for solutions in which the initial concentration of peroxide was considerably less than that of dissolved hydrogen. In these cases no significant amount of oxygen appeared in the solution. The peroxide concentration decreased at a rate which became greater after reaction proceeded. Then when the peroxide concentration approached zero, the rate fell abruptly, and a steady-state peroxide concentration was reached at levels of the order of 1  $\mu\text{M/liter}$ . Figure 12 shows results obtained from solutions where the initial hydrogen and peroxide concentrations were comparable. With equal concentrations, a steady state was reached at somewhat greater peroxide concentrations, comparable to the steady states reached on exposures of pure water in the pile for periods of 2 minutes to 1 hour. When considerable excess peroxide was present, the steady state concentration of hydrogen rapidly increased as shown by the curves in Figure 13. Appreciable amounts of oxygen began to appear when the hydrogen and peroxide concentrations were equal, and such oxygen was formed when peroxide was in excess.

The results on the solutions with hydrogen in excess show that a small concentration of added hydrogen should be sufficient to suppress almost completely the decomposition of water under pile radiation. This was verified by exposing water saturated with hydrogen at 1 atm. in the pile. As shown in Figure 14, no appreciable oxygen or peroxide appeared in this solution. A small drop in the dissolved hydrogen concentration on exposure must be ascribed to absorption of hydrogen by the silica walls of the vessel. The suppression of water decomposition by small amounts of hydrogen may become

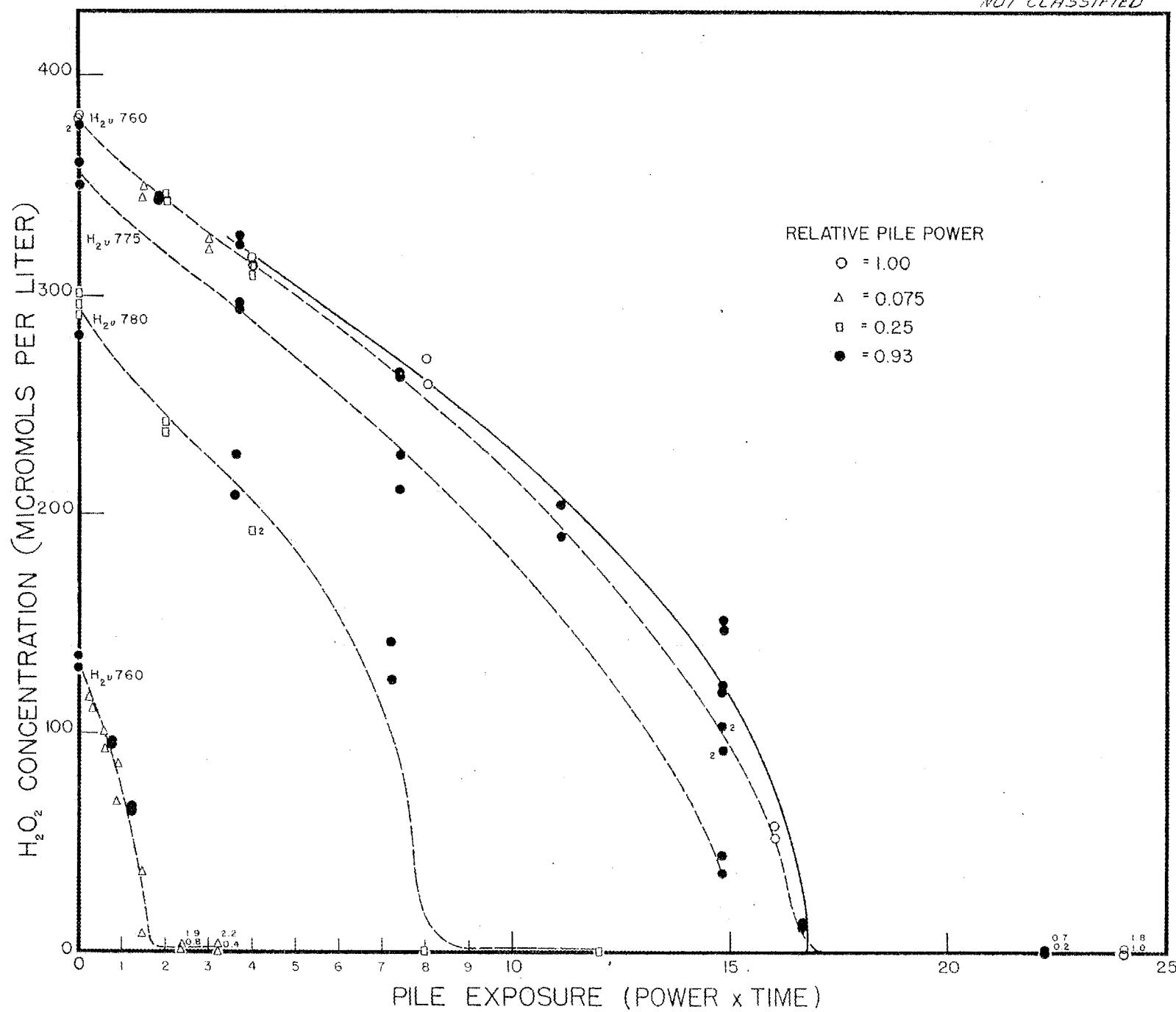


FIG.II. REACTION BETWEEN DISSOLVED H<sub>2</sub>O<sub>2</sub> AND EXCESS H<sub>2</sub> UNDER  
PILE EXPOSURE

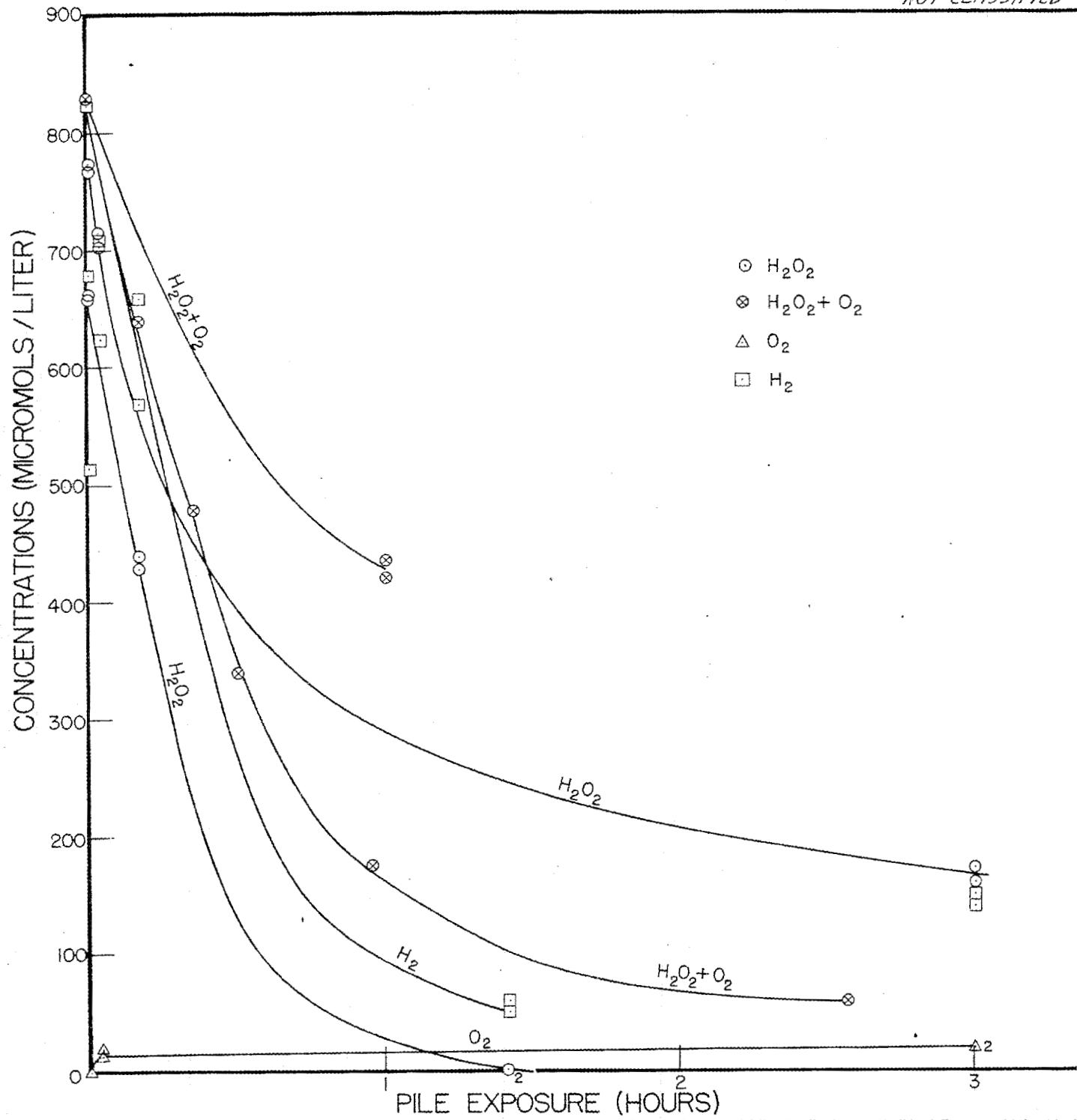


FIG. 12. DECOMPOSITION OF WATER IN SOLUTIONS CONTAINING COMPARABLE AMOUNTS OF  $H_2$  AND  $H_2O_2$

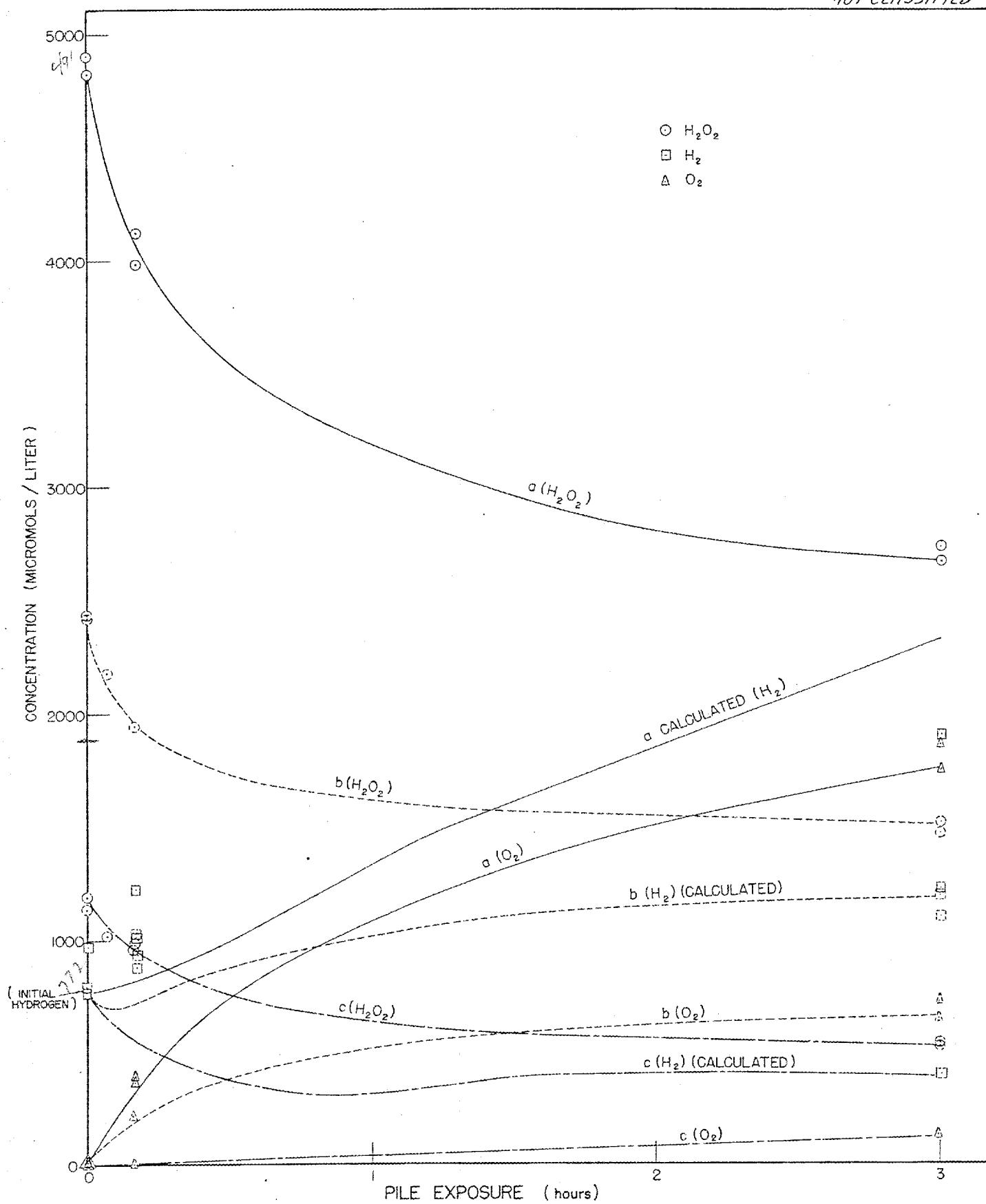
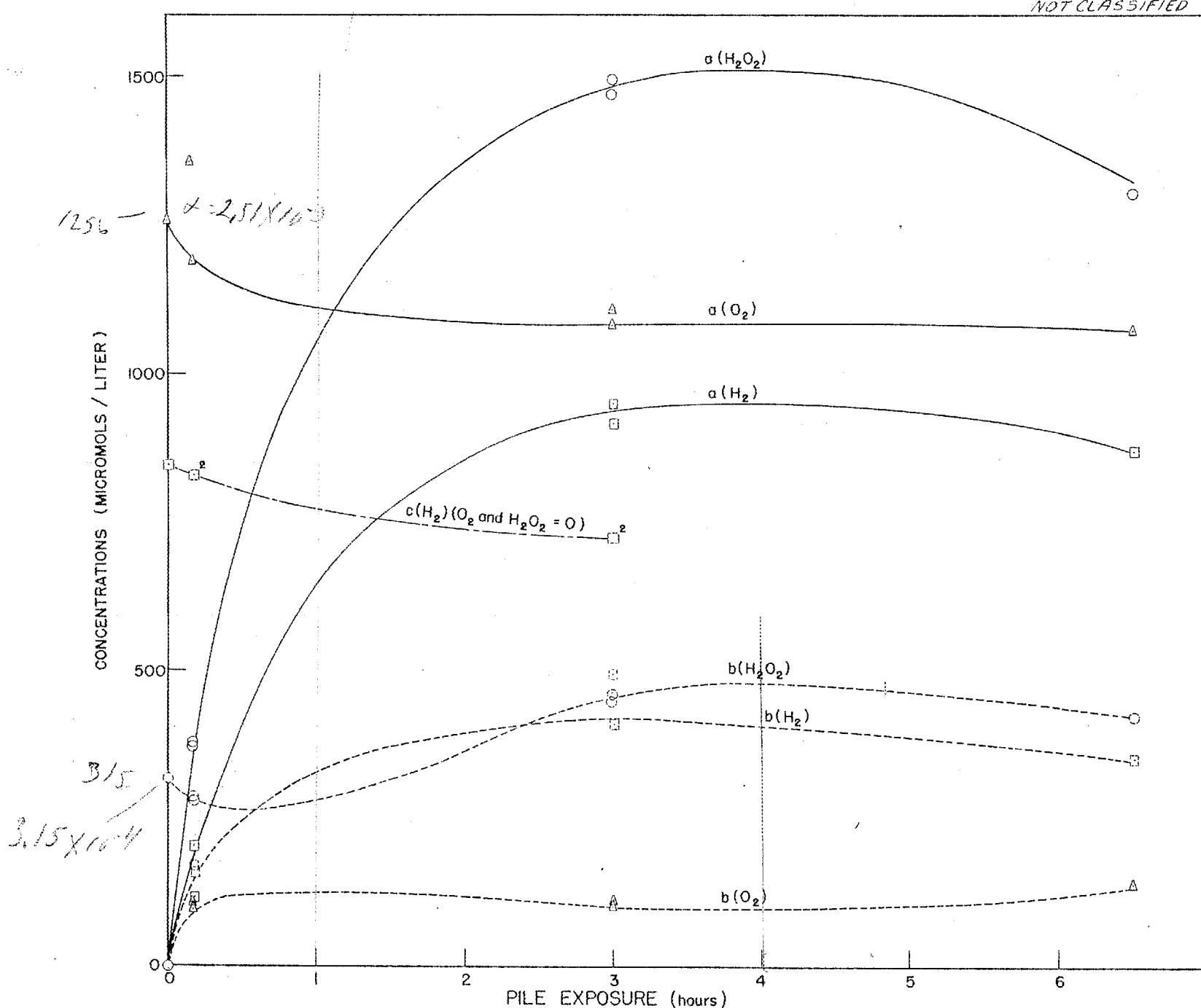


FIGURE 13. DECOMPOSITION OF WATER IN SOLUTIONS CONTAINING HYDROGEN AND PEROXIDE WHEN PEROXIDE IS IN EXCESS.



of some importance in the technology of water-cooled and water-moderated reactors.

Figure 14 also shows the decomposition of water in solutions containing initially only hydrogen peroxide and only oxygen. In these cases, more hydrogen was formed than from water initially not containing any dissolved products.

The results thus show that excess hydrogen almost entirely suppresses the decomposition of water in the pile, but excess peroxide instead of suppressing the decomposition has the opposite effect; the higher the excess of peroxide, the more hydrogen is present at the steady state. Thus, hydrogen peroxide plays a double role in the back reaction; it is, of course, a reagent necessary for the back reaction to occur, but it also, like many other solutes, acts as an inhibitor for the back reaction. The inhibiting action of hydrogen peroxide is clearly shown from the increase in rate as the peroxide concentration drops indicated by the data of Figure 11. Figure 15 shows that in a series of solutions, all containing the same concentration of dissolved hydrogen (saturated at atmosphere pressure), but different concentrations of peroxide, the initial rate of peroxide disappearance is greater the smaller the peroxide concentration. Figure 16 shows that when we consider the hydrogen and peroxide concentrations finally attained at the steady state for solutions of differing initial compositions, the hydrogen concentration is higher the greater the peroxide concentration. Various ways of considering the results all lead to the same conclusion; that hydrogen peroxide is a marked inhibitor for the back reaction. This is the explanation for the previously observed fact that, starting with pure water, a higher steady-state concentration of hydrogen is observed when a considerable space is available over the water than when the vessel is full. In the former case, most of the

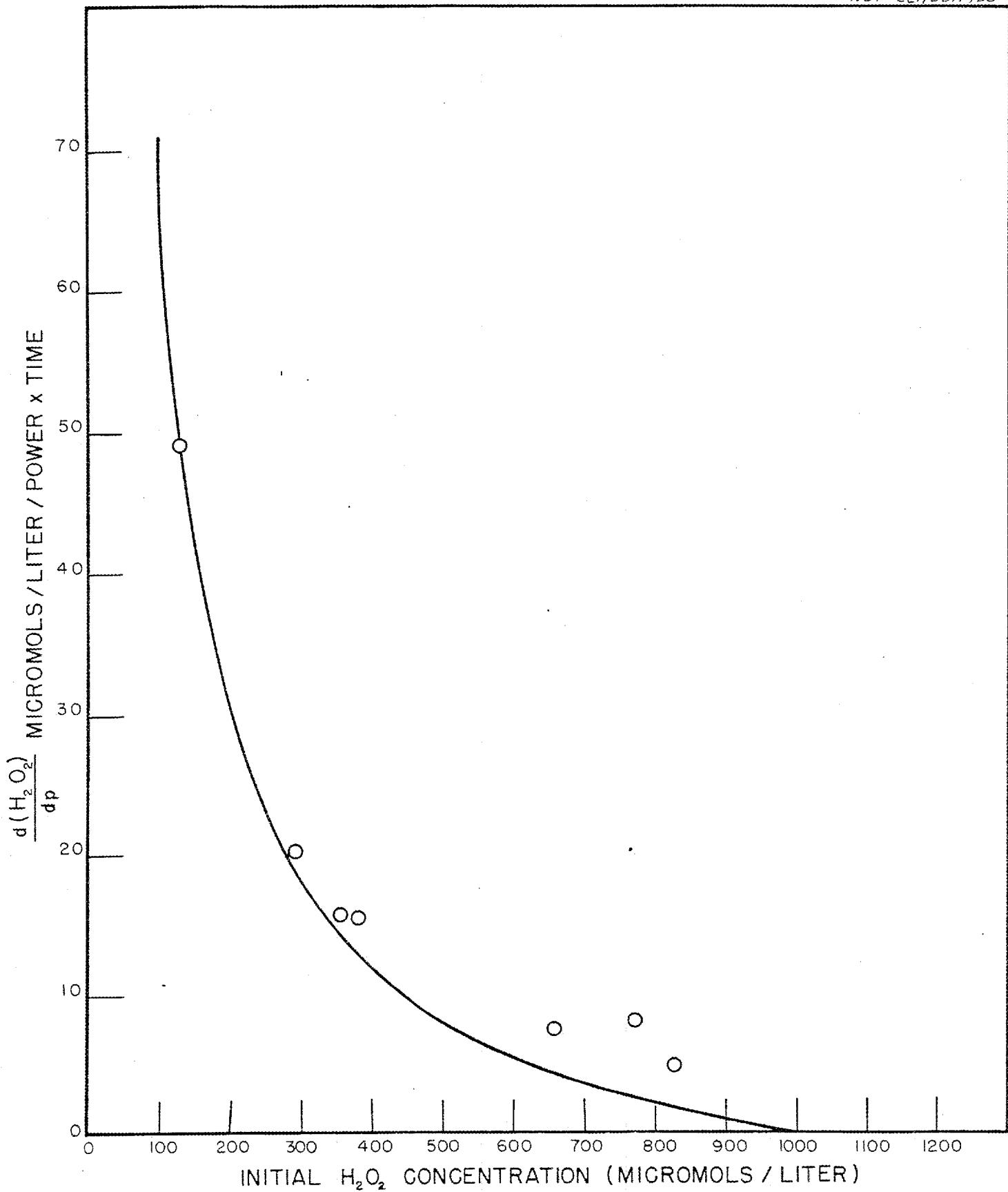
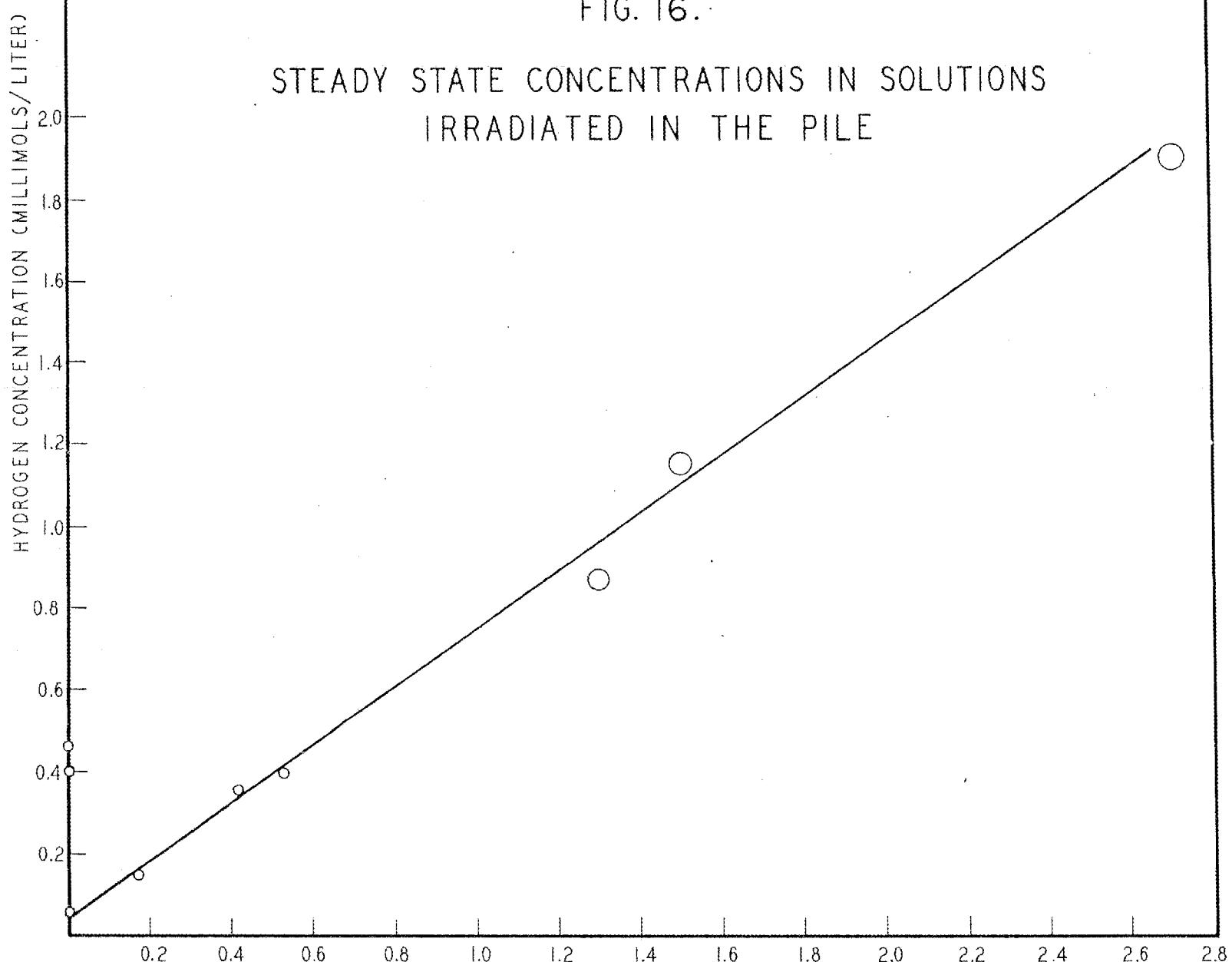


FIG. 15. INITIAL RATE OF PEROXIDE DISAPPEARANCE IN HYDROGEN SATURATED SOLUTIONS

FIG. 16.

STEADY STATE CONCENTRATIONS IN SOLUTIONS  
IRRADIATED IN THE PILE

hydrogen formed escapes into the gas phase, leaving an excess of peroxide in the solution which inhibits back reaction and causes the hydrogen over-oxidation and thereby the pressure to rise to high levels. Since excess peroxide inhibits the back reaction, a solution containing large peroxide excess would presumably decompose under radiation indefinitely if it were not for the decomposition of peroxide by oxygen which occurs at the same time. The evolution of hydrogen stops when the pressure level has been sufficiently reduced by the decomposition to oxygen.

For solutions containing excess hydrogen, the material balances were good; since no appreciable amount of oxygen remained, plots of the hydrogen and peroxide concentrations against time in any run would show parallel curves. The material balance in these runs is shown in Table 6. In view of the latter runs, only peroxide was determined, since it represents almost all of the dissolved hydrogen. The runs with excess oxygen, the unbalance balances were not as satisfactory. The curves given in Figure 15 and in the report of dissolved hydrogen are calculated from the oxygen and peroxide ratios in the assumption of zeroth order behavior, and the degree of experimental unbalance can be determined from the deviation of the measured hydrogen points on the graph from the calculated hydrogen curve.

For solutions with excess hydrogen, runs were made at several radiation rates to see if there was an inhibitory effect on the reaction. The rates are plotted as peroxide concentration versus total dose supposed to represent doses of total accumulated pile assembly output. If the rate of the reactions were directly proportional to the radiation intensity, points at different powers would all lie on the same curve. The data do not appear to be separated enough to decide definitely whether any deviation from such proportionality exists. A slight deviation is suggested in the direction of increasing oxygen yield (amount of reaction per unit energy input) with increasing intensity.



### V. DISCUSSION

The mechanism by which the decomposition of water is affected by various types of radiation was briefly discussed in the Introduction. Ionization or ionisation of the water molecules leads ordinarily to bond breaking with the formation of the free radicals OH and H. In regions of high ionization density, such as the tracks of proton racets or very slow electrons, radicals are formed in high concentration. Many will react with one another to form the molecule  $H_2O_2$  and  $H_2$  before they have time to separate by diffusion into the bulk of the water. In regions of lower ionization density such as the tracks of fast electrons, most of the radicals will diffuse out into the water before they have a chance to react with one another. The system therefore behaves as though two different reactions were occurring simultaneously:

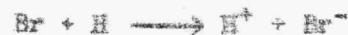


It is possible that in regions of high ionization density, electronically excited molecules may react with one another to form molecular  $H_2$  and  $H_2O_2$  directly, thereby giving an additional contribution to reaction 1. The free radicals formed by reaction 2 disperse through the water by diffusion and are available to react with dissolved materials. Since H is a strong reducing agent and OH a strong oxidizing agent, oxidation-reduction reactions are common in irradiated solutions. Existence of the radiation-induced back reaction between dissolved  $H_2$  and  $H_2O_2$  shows that the radicals can utilize hydrogen and reduce peroxide:



When both  $H_2$  and  $H_2O_2$  are present, a chain reaction will evidently be set

up. This reaction is completely analogous to the well-known gaseous chain reaction between hydrogen and chlorine; here the place of Cl is taken by OH which has very similar chemical properties. The presence of readily oxidized material such as bromide ion will remove free radicals from the system and thereby interrupt the back reaction chain. The probable reactions occurring with bromide ion are



The bromide ions therefore act as catalysts for the recombination of radicals to water. We would expect most oxidation-reduction systems to behave in the same way. Anions containing oxygen probably interrupt the back reaction by a similar mechanism with peroxy radicals playing the role of the oxidized state.



While solutes interrupt the back reaction, they can have no effect on the forward reaction which takes place in the minute regions of high ionization density. The production of hydrogen and peroxide in the solution therefore proceeds uninterrupted until the concentration of these decomposition products becomes high enough for them to compete effectively with the foreign solutes for reaction with the radicals. The initial rate of hydrogen gas formation is therefore the same for all solutions (Table 4).

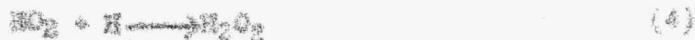
Excess peroxide also inhibits the reaction by interrupting the chain. The reaction in this case is the same one by which peroxide is oxidized to oxygen:



When many OH radicals are present, the resulting HO<sub>2</sub> radical can be oxidized further to oxygen.



However, the HO<sub>2</sub> can also be reduced back to hydrogen peroxide.



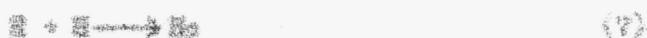
The sum of reactions (3) and (4) is again simply the combination of H and OH to water, so that excess peroxide acts in the same way that bromide ion does to inhibit the back reaction. When reaction (5) occurs the resulting oxygen can also be reduced back to HO<sub>2</sub>.



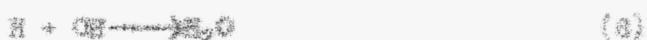
Reactions (5) and (6) are another oxidation-reduction pair, so that oxygen as well as HO<sub>2</sub> will be expected to act as a back reaction inhibitor.

When hydrogen is present in excess, reaction (8) apparently does not occur to any important extent since no appreciable quantity of oxygen is produced. The excess hydrogen keeps down the concentration of OH by reaction (2) so that most of the radicals are in the form of H and reaction (4) is favored over (5).

From oxygen terms, the kinetics expected from the above equations are too complicated to admit of a good theoretical treatment. Moreover, the catalysis of peroxide decomposition by metals indicates that the rate of reaction (4) is probably not reproducible. Systems containing excess hydrogen are, however, to be treated theoretically by considering reactions (7), (8), (1), (2), (3) and (4) above, together with the radical recombination reactions



and



The reaction of OH with OI is neglected because, in these systems, the OI concentration is much lower than that of H, and the combination of two

OH's probably requires some activation energy because of the dipole repulsion which must exist between two OH radicals if they come together in the proper orientation to form  $H_2O_2$ .

It is assumed in the following treatment that the reaction radicals are dispersed uniformly throughout the solution so that the rates of their reactions are proportional to their concentrations in the usual way. We assume, following the usual procedure, that the rate of change of radical concentrations is small compared to the rates of the individual reactions involving radicals and may therefore be set equal to zero. At relatively high concentrations of  $H_2O_2$  we may expect that most of the radicals will disappear by reactions (3) and (4) so that reactions (1) and (2) may be neglected. We note that (3) followed by (4) does not change the  $H_2O_2$  concentration. Then, if we let  $I$  be the radiation intensity, and  $k$  with an appropriate subscript the rate constant for any of the above reactions:

$$(A) \quad -\frac{d(H_2O_2)}{dt} = k_1(I)(H_2O_2) + k_2(I)$$

$$(B) \quad -\frac{d(H_2)}{dt} = k_3(I)(H_2) + k_4(I)(H_2O_2) + k_5(I)$$

$$(C) \quad \frac{d(OH)}{dt} = 0 + k_6(I) + k_7(I)(H_2O_2) + k_8(OH)(H_2) + k_9(OH)(H_2O_2)$$

$$(D) \quad \frac{d(OH)}{dt} = 0 + k_{10}(I) + k_{11}(I)(H_2O_2) + k_{12}(OH)(H_2) + k_{13}(OH)(H_2O_2)$$

Since

$$k_9(OH)(H_2O_2) = k_{13}(OH)(H_2O_2)$$

(because  $H_2O_2$  must be consumed as fast as it is formed) we have from (C) + (D):

$$0 = 2k_{10}(I) + 2k_{12}(OH)(H_2O_2)$$

and setting (A) = (B), we obtain:

$$\frac{(OH)}{(OH)} = \frac{k_6(I)}{k_3(H_2)} = \frac{k_7(I)(H_2O_2)}{k_4(H_2)}$$

$$(E) \quad k_1(H) = \frac{k_2 k_R I(H_2)}{k_3 (H_2O_2)^2}$$

Substituting in A

$$(F) \quad \frac{-d(H_2O_2)}{dt} = \frac{k_2 k_R I(H_2)}{k_3 (H_2O_2)} - k_p I$$

On integrating between the limits  $(H_2O_2)_1$  at  $t = t_1$  and  $(H_2O_2)$  at  $t = t$ , we obtain:

$$(G) \quad \frac{(H_2O_2) - (H_2O_2)_1}{b} + \frac{a}{b^2} \ln \frac{a + b(H_2O_2)_1}{a + b(H_2O_2)} = t - t_1$$

where  $a = \frac{-k_2 k_R I}{k_3}$ ;  $b = k_p I - \frac{k_2 k_R I}{k_3}$

$$C = (H_2) - (H_2O_2)$$

The one quantity appearing in the above equations which is already known is  $k_p I$ . This is the rate at which hydrogen is formed in solutions of active solutes such as BDI in which radicals are destroyed by the solute. If we express the radiation intensity in arbitrary units of g/cm power and set  $k_R I = 2.2$   $\mu\text{moles}/\text{liter, minute}$  at a radiation power of 1.0

If we try to fit equation (G) to the experimental data shown in Figure 11 for the highest peroxide concentration, we obtain the solid curve using the values  $(H_2O_2)_1 = 326$ ,  $t_1 = 0.875$ ,  $C = 360$ ,  $k_2 k_R / k_3 = 0.42$ ,  $I = 1$  where the concentration unit is  $\mu\text{moles/liter}$ , the time unit minutes.

We note that this equation fits the data fairly well over most of the range. However, the initial rapid rate at  $(H_2O_2) = 360$  cannot be explained by this mechanism. Also, as the peroxide concentration approaches zero, the rate of peroxide removal approaches infinity as shown by equation (F). Experimentally,

we find that at very low peroxide concentrations the rate of removal suddenly decreases and we reach a steady state peroxide concentration at around 1 micro-mole/liter. Looking at equation (E), we see that as the peroxide concentration approaches zero, the hydrogen atom concentration becomes infinite. Reactions (7) and (8) must then be important. Including these reactions, one obtains:

$$(H) \frac{-d(H_2O_2)}{dt} = k_1(H)(H_2O_2) - k_3I$$

$$(J) \frac{-d(H_2)}{dt} = k_2(OH)(H_2) + k_7(H)^2 - k_3I$$

$$(K) \frac{d(I)}{dt} = 0 = k_3I - k_1(H)(H_2O_2) + k_2(OH)(H_2) - k_4(H)(HO_2) - 2k_7(H)^2 - k_9(H)(OH)$$

$$(L) \frac{d(OH)}{dt} = 0 = k_7(H)^2 + k_1(H)(H_2O_2) - k_2(OH)(H_2) + k_8(OH)(HO_2) + k_9(H)(OH)$$

$$(J) + (L): k_3I - k_2(OH)(H_2O_2) - k_8(H)(OH) + k_7(H)^2 = 0$$

From (J) = (L), or by setting (H) = (J), we find:

$$(OH) = \frac{k_7(H)^2 + k_1(H)(H_2O_2)}{k_2(H_2)}$$

Combining the last two equations, we get:

$$(M) [k_1(H)]^2 + [k_1(H)]^2 \left[ \left( \frac{k_1 k_3}{k_2} + \frac{k_1^2}{k_7} \right) (HO_2) + \frac{k_1 k_2 (k_3)}{k_2} \right] + k_1(H) \left[ \frac{k_1^2 k_3}{k_2 k_7} (H_2O_2)^2 \right] - \frac{k_1^2 k_2 k_3 I (H_2)}{k_2 k_7} = 0$$

We now attempt to fit the observed kinetics by the use of equation (M).

The experimental curves representing peroxide concentration as a function of exposure in the presence of excess hydrogen (Figure 1) have a very peculiar

shown. They fall more and more steeply as the product concentration increases and then suddenly level off and level out at very low product values. As shown from equation (2) that  $\dot{R}_2(R_1)$  is proportional to  $R_1^2$ , the initial rate of disappearance of  $R_2$  in terms of  $\frac{\dot{R}_2(R_1)}{R_1}$  should be fitted to the observed data. Here an overall reaction rate of  $R_1$  is taken, since it is not possible to distinguish between the different rates and thus introduce the two separate contributions and eliminate the reaction rate of  $R_2$  as a parameter of  $\dot{R}_2(R_1)$ .

The data of  $R_1$  and  $\dot{R}_2(R_1)$  obtained under the conditions of the first series of experiments are given below. The calculated values of  $\dot{R}_2(R_1)$  are also given in the table. The remaining values are obtained by the method of successive approximations. The remaining values are obtained by the method of successive approximations. The remaining values are obtained by the method of successive approximations. The remaining values are obtained by the method of successive approximations.



Equation (2) for  $\dot{R}_2(R_1)$  vs.  $R_1$

$$(2) \quad \left[ \dot{R}_2(R_1)^2 + 2.7(\dot{R}_2(R_1))^2 R_1^2 + 0.45R_1^2 \dot{R}_2(R_1)^2 + 17.2R_1^2 \dot{R}_2(R_1)^2 \right] \\ + 1.2R_1^2 \dot{R}_2(R_1) = 0.$$

The initial value of  $\dot{R}_2(R_1)$  can be determined from the first term of equation (2) obtained from this relation by the following approximation. This is a very accurate value because the constant in this term is based on many observations.

The calculated values of  $\dot{R}_2(R_1)$  for the first series of experiments are given in the following table. The corresponding values of  $R_1$  are given in the table.

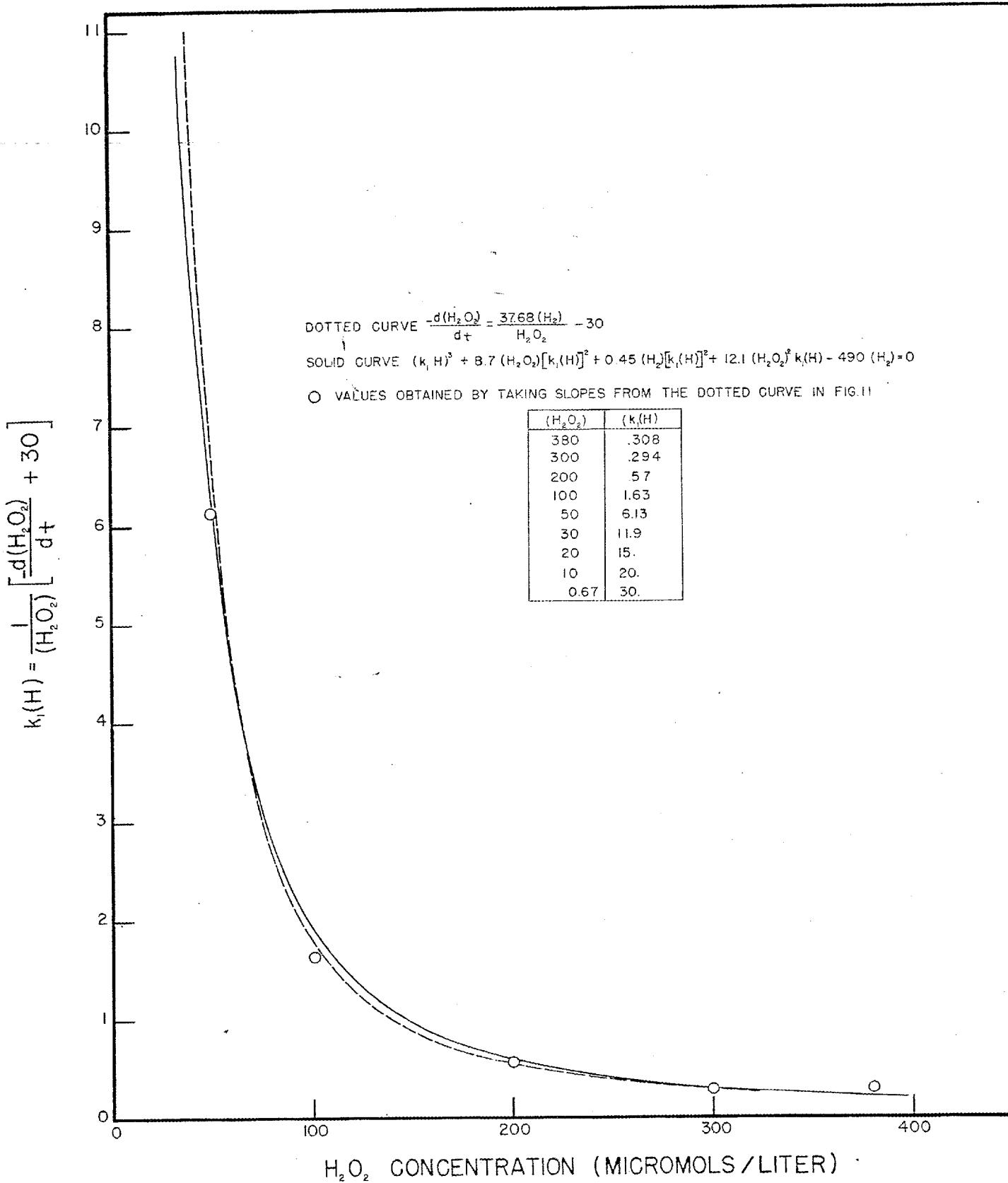


FIG. 17. PLOT OF  $k_i(H)$  VS.  $(H_2O_2)$  FOR INITIAL  $(H_2O_2) = 380$ ,  $(H_2) = 760$  AT RELATIVE POWER 1.0

low peroxide concentrations where curve F goes to infinity at  $(H_2O_2) = 0$  and curve M goes to  $k_1(H) = 30$  at  $H_2O_2 = 0.67$ , which is approximately the steady-state value. Thus at  $H_2O_2$  concentrations above  $50 \mu\text{M}$ , the data are fit just as well if the radical recombination reactions (7) and (8) are neglected. We conclude that at higher concentrations all  $\text{H}$  and  $\text{OH}$  radicals disappear by reactions (3) and (4).

The initial rates (Figure 11) are slightly more rapid than expected from the subsequent behavior. This is probably ascribable to presence of a trace of organic impurity in the solutions, which is used up by reaction with oxidizing free radicals in the course of the first two or three minutes of exposure.

By use of the above constants, one can calculate the initial rate for runs in which the hydrogen concentration was that corresponding to saturation at atmospheric pressure and the peroxide concentration was varied. The resulting theoretical curve has been drawn in Figure 15 for comparison with the observed data. The curve is practically the same whether equation (F) or equation (M) is used.

Reliable values for the individual rate constants cannot be obtained since much latitude exists in the determination of the constants in equation (M).

The plot, Figure 16, of the concentration of hydrogen versus that of hydrogen peroxide at the steady state for solutions initially containing excess peroxide appears to be linear. Since oxygen is present in the solutions, it seems impossible to work out a reasonably simple theory, and it may be that the apparent linearity in this case has no particular theoretical significance.

The above reaction scheme for water decomposition appears to describe the situation with fair quantitative precision in those cases where quantitative treatment is possible, and to give an adequate qualitative explanation for

the observed behavior in other situations. We believe that the reaction scheme here proposed can be regarded with considerable confidence.

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