CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION

UNCLASSIFIED

ORNL 128
CHEMISTRY-RADIATION &
RADIOCHEMISTRY

OAK RIDGE NATIONAL LABORATORY LIBRARY
3 4456 0024020 0

CHEMISTRY DIVISION

DECOMPOSITION OF TRITIUM OXIDE UNDER ITS OWN RADIATION

J. A. GHORMLEY

A. O. ALLEN

CENTRAL RESEARCH LIBRARY
DOCUMENT COLLECTION
LIBRARY LOAN COPY
DO NOT TRANSFER TO ANOTHER PERSON
If you wish someone else to see this document, send in name with document and the library will arrange a loan.

OAK RIDGE NATIONAL LABORATORY

OPERATED BY
CARBIDE AND CARBON CHEMICALS CORPORATION
FOR THE
ATOMIC ENERGY COMMISSION
POST OFFICE BOX P
OAK RIDGE, TENNESSEE

UNCLASSIFIED

This document consists 25 pages.
Copy 8 of 102 Series A.

ISSUED: Training School Library

ORNL-128

OAK RIDGE NATIONAL LABORATORY

Contract No. ~~AT-33-1-GEN-53~~
7405-eng-26

CHEMISTRY DIVISION

DECOMPOSITION OF TRITIUM OXIDE UNDER ITS OWN RADIATION

J. A. Ghormley

A. O. Allen

September 1, 1948

OAK RIDGE NATIONAL LABORATORY LIBRARY

3 4456 0024020 0

Date Received: 9/9/48

Date Issued: OCT 4 1948

ORNL-128
Chemistry-Radiation and Radiochemist

DISTRIBUTION:

1. G. T. Felbeck (C&CCC N.Y.-N.Y.)
2-4. 706-A Library
5. 706-B Library
6. Biology Library
7. Health Physics Library
8. Training School Library
9-13. Central Files
14. D. C. Bardwell
15. C. D. Cagle
16. J. A. Cox
17. E. B. Ashcraft
18. A. Hollaender
19. J. H. Frye, Jr.
20. E. J. Murphy
21. M. D. Peterson
22. C. N. Rucker
23. J. C. Stewart
24. A. M. Weinberg
25. J. A. Lane
26. F. L. Steahly
27. S. R. Sapirie (AEC-Townsite)
28. H. M. Roth (AEC-Townsite)
29-37. D. C. Bardwell
38-43. Argonne National Laboratory
44-45. Atomic Energy Commission, Washington
46-51. Brookhaven National Laboratory
52-53. Carbide & Carbon Chemicals Corporation (K-25 Area)
54. Columbia University (Failla)
55-58. General Electric Company
59-65. Hanford Directed Operations
66. Iowa State College
67-68. Kellex Corporation
69-71. Los Alamos
72-73. Monsanto Chemical Company, Dayton
74-75. National Bureau of Standards
76. Naval Radiological Defense Laboratory
77. NEPA
78-79. New York Directed Operations
80. Patent Advisor, Washington
81-95. Technical Information Division, ORDO
96-100. University of California Radiation Laboratory
101-102. University of Rochester

ABSTRACT

Water in which 2 to 19% of the hydrogen is replaced by tritium decomposes into hydrogen and oxygen as a result of bombardment by the tritium beta rays. The decomposition stops as a result of back reaction when the pressure of gaseous products reaches values which vary from 20 to 600 or more cm. Hg, depending apparently on the nature and amount of impurities present. The steady-state pressure of electrolytic gas is generally lowered by increase of temperature (to an extent varying for different samples) and by exposure to gamma rays. The decomposition continues when the water is frozen and kept at liquid nitrogen temperature. He^3 formed by tritium decay diffuses through the walls of fused silica vessels, but not through soft glass; and the activity of a tritium oxide sample can readily be determined by collecting and measuring the pure helium which comes out through the walls of a silica container.

I. INTRODUCTION

Study of the decomposition of water by alpha rays and by X-rays has shown a profound difference between the effect of these two types of radiation. With alpha rays, decomposition progresses smoothly to yield hydrogen[1]; with X-rays, apparently no decomposition is observed[2]. In work done at the Metallurgical Laboratory during the war, we have shown that the apparent lack of decomposition by X-rays is due to a rapid back reaction between the decomposition products, hydrogen and hydrogen peroxide, to re-form water[3]. A steady state results in which very little of the products are present in the water, and without very careful examination, no decomposition appears to occur. With alpha rays, the back reaction seems to be very much slower relative to the decomposition than with X-rays, so that the resulting steady state, if it exists at all, must occur only when the concentration of hydrogen dissolved in the water has reached a much higher level than that attained in published experiments. The difference between these two types of radiation is ascribed to the difference in density of free radical formation along the track of the radiations[4]. With the fast electrons produced by X-rays, radicals are formed far apart and mostly diffuse out into the body of the solution where they can react with dissolved product molecules and thereby induce back reaction. With alpha rays, where the radicals are formed much closer together, they presumably react with one another before they have a chance to diffuse out into the solution, so that the back reaction is much less important. With radiations of intermediate energy loss density, one might therefore expect a steady-state level higher than that found with X-rays, but still lying in an

easily obtainable range. Indications have been found that this situation holds for cyclotron deuterons[4].

The beta rays from tritium possess an average energy of about 5.6 kev, and the ionization density along their tracks is comparable to that of cyclotron deuterons. We therefore, expected that under bombardment by these electrons, tritium oxide should decompose to a measurable extent before the reaction arrested itself. Information on this point would be valuable to those who are interested in the handling and transportation of tritium oxide.

A supply of a few cc of impure tritium (contaminated, that is, with ordinary hydrogen) was available on the laboratory site for these experiments. Because of the small quantity, the experiments were done on a micro scale.

II. EXPERIMENTAL METHODS

1. Preparation of tritium oxide. The tritium gas was supplied sealed in pyrex bulbs, each of which contained an amount of tritium of the order of 1 curie. The percentage of tritium in the total hydrogen present, $(T/(T + H)) \times 100$, was 2% for the material used for water ampoule 1, 4% for ampoules 3 and 9, 15% for ampoules 4 and 5 and 19% for ampoules 2, 6 and 7. The tritium bulbs were broken inside a vacuum line and the gas passed through a heated palladium thimble to remove any foreign gases. The hydrogen gas was converted to water by one of two methods. In the first method, the gas was simply allowed to come into contact with heated copper oxide, and the resulting water was frozen out. This method was abandoned when it was found that the resulting water might be contaminated with traces of entrained copper oxide. In the second method, pure oxygen derived from heating potassium permanganate was in contact with the palladium thimble; as soon as the gas passed through the hot palladium, it was immediately oxidized by catalysis on the palladium surface.

In both methods the water was condensed into a small fused silica capillary, connected with a pyrex vacuum line through a graded seal. The capillaries were

0.6 mm inside diameter and were drawn down at one end to a diameter of about 0.2 mm. After the water had condensed into the capillary under liquid nitrogen, the capillary was sealed off. The resulting ampoule consisted of a wider portion about 1 cm long and a narrower portion about 2 cm long. The decomposition of the water under its own radiation was followed by determining the pressure in this capillary by the method described in the next section.

Although every effort was made to exclude stopcock grease and mercury from the part of the vacuum system containing the ampoule, microscopic examination of the samples showed the presence of particles of foreign matter. This seemed impossible to avoid, since any volatile substance present in any part of the vacuum system would condense into the ampoule along with the water when the ampoule was cooled with liquid nitrogen. In two of the ampoules, numbers 9 and 11, water was condensed on the wall of the tube above the ampoule; the tubing was then sealed off from the rest of the line and the water distilled into the capillary part. The capillary was then rinsed out; it was warmed, thus forcing the water back into the larger portion of the tubing, then the water was distilled back into it, and this process was repeated several times. Finally, about 2/3 of the water was distilled into the capillary, which was then sealed off. This procedure probably got rid of most of the impurities.

Although the inner surface of the fused silica capillary was subjected to very intense bombardment by the weak beta rays, no color was noticed in the glass. The effect of bombardment on the silica became evident in the case of one ampoule by the formation of large pits in the wall, very readily visible under low power magnification and having depths as great as several hundredths of a mm. With the other ampoules, this pitting did not appear.

One of the ampoules was made of lead glass in order to avoid the outward diffusion of He^3 which occurred with fused silica (next section). The inner

layer of this glass turned milky on heating, probably indicating that it had been attacked by radiation.

The water, or the layer of glass immediately surrounding it, exhibited a glow barely visible at room temperature in the dark. On cooling to liquid nitrogen temperature, the intensity of the glow increased considerably.

Because of its extremely weak radiation, tritium is considered safe to handle in amounts up to 1 curie. The quartz capillary ampoules will withstand very high internal pressures and will not crack under thermal shock; they were handled with impunity and no breakage occurred. The lead glass ampoule did finally crack when it was warmed in an oven, but the precaution had been taken of sealing this ampoule within a larger tube, so that no escape of tritium occurred. Glass tubing through which tritium or tritium water had been passed was found to retain considerable activity by adsorption, and was generally discarded after it had been used once. Small pieces of a pyrex tube in which tritium had been stored conveniently yielded tracer amounts of tritium on heating even after exposure to the atmosphere for several months.

2. Measurements. The pressure in the ampoules was determined by measurement of the boiling point of the water in the ampoule. The method as applied to larger ampoules is described elsewhere[5]. In the present case, the water was first centrifuged into the small-diameter end. A bubble was formed in the tip by freezing in liquid nitrogen followed by gentle warming with the flame. The end of the ampoule containing the water was then placed in a bath of warm glycerin while the upper end containing the gas was cooled with ice. When the temperature of the water in the small end reached the boiling point under the pressure of the gas in the upper end, the bubble began to grow and the water moved upward. Temperature readings of the glycerin bath were taken when the meniscus marking the upper end of the bubble reached a distance of 0.25 cm. from the end of the capillary and again when this distance reached 0.5 cm. The bath

was then allowed to cool and the temperatures again noted at which these distances were attained; the whole process was repeated several times, and average values of the temperatures giving these distances were used. The two temperatures were usually separated by an interval of about 2°. The fact that the water did not immediately rise completely out of the high temperature zone as soon as the boiling point was reached is ascribed to the presence of some permanent gas in the bubble. Pressure in the bubble is essentially equal to the pressure of the main body of gas in the cooled part; but it is made up of the vapor pressure, P_v, plus the unknown pressure of the permanent gas in the bubble, P_g. If V_1 and V_2 are the bubble volumes at temperatures T_1 and T_2, we have for the total pressures P_1 and P_2:

$$P_1 = P_g + P_{v_1} \qquad (1)$$

$$P_2 = P_g(V_1/V_2) + P_{v_2} \qquad (2)$$

If we assume that the change in pressure of the main body of the gas (due to compression when the water slug is raised by expansion of the bubble) is negligible, we equate P_1 and P_2; and since $V_2/V_1 = 2$, we find

$$P_1 = P_2 = 2P_{v_2} - P_{v_1} = P_{v_2} + (P_{v_2} - P_{v_1})$$

Thus, the gas pressure in the ampoule is given by the vapor pressure of water at the higher of the two temperatures plus the difference in vapor pressures at the two temperatures. In practice, over the small temperature range involved between T_2 and T_1, the vapor pressure may be taken as proportional to the temperature, so that the pressure as recorded was taken as the vapor pressure of water at a temperature equal to $T_2 + (T_2 - T_1)$. Actually P_1 and P_2 will not be exactly equal because of the compression. The true pressure, therefore, may

be lower than that recorded by a few per cent. The vapor pressure of water containing 15% of tritium must be a little lower than the values for ordinary water which were used in the calculation, but this error is small compared to other errors. The relative values of different determinations on the same ampoule are reliable to better than 5%, but the absolute values may be low by a somewhat greater percentage.

The volume of the gas and liquid phases within the ampoules was determined by measurement of the diameter at different points along the capillary, by a microscope with a micrometer eye-piece; lengths along the capillary were determined by means of a travelling microscope stage with vernier.

Some of the ampoules were eventually broken open in a vacuum system at liquid nitrogen temperatures , and an aliquot of the gas obtained was analyzed for hydrogen, oxygen, and inert gas assumed to be He^3 formed by beta decay of tritium. The method of analysis is described elsewhere. The gas was kept at a pressure of less than 10^{-3} mm in the McLeod gauge. Low pressures of gas were required to permit rapid diffusion between the McLeod gauge and the remainder of the analysis system. Hydrogen and oxygen were determined by the pressure drop which resulted from combustion on a heated platinum filament. Excess hydrogen or oxygen was determined by adding pure oxygen or hydrogen from another part of the system and running another combustion, and He^3 was finally found by difference.

An attempt was made to determine the amount of tritium activity in a sample by introducing a small aliquot of the sample in the form of water vapor, or of hydrogen gas, into an ionization chamber; the results were unreliable because of the adsorption of tritium on the walls of the chamber. The method was not used, although it probably could have been made reliable by proper use of carrier hydrogen in the chamber.

A simple reliable method for determining the amount of tritium activity in a

water ampoule was based on the rate of helium formation in the ampoule. As described in detail in the next section, it was found that helium diffuses readily through the silica walls of these ampoules, but was retained for long periods in vessels of soft glass. After the water sample had been sealed up for some time in the silica ampoule, a steady state was reached in which helium diffused out of the ampoule at the same rate at which it was being formed within. Consequently all that was necessary to determine the activity was to place the ampoule in an evacuated soft glass bulb and measure the amount of gas produced from time to time by means of a McLeod gauge. This gas consisted entirely of helium, since none of it was removed by contact with heated metallic calcium.

The activity in some of the ampoules was determined by calorimetric measurement of the heat generated by the beta decay. These measurements were performed by G. H. Jenks. A description of the calorimeter and the measurements of the average energy of the tritium beta will be published by Dr. Jenks in a forthcoming report. To convert the rate of heat production (measured in watts) to curies of tritium, we used the figure 5.6 kev for the average energy of the tritium beta particle.

III. RESULTS

1. Diffusion of helium through the quartz ampoule. Analysis of the gas present in the ampoules showed the amount of helium to be very much smaller than expected from the activity thought to be present. On reference to the literature, it was found that the rate of diffusion of helium through fused silica is much greater than that of other gases, and is also much greater than its diffusion rate through other kinds of glass[6]. A tritium oxide ampoule was accordingly placed within an evacuated soft glass bulb connected to a McLeod gauge, and gas which was not absorbed by hot metallic calcium was found to accumulate in the bulb. The rate of helium accumulation in the bulb was found to be independent of time after the ampoule had been sealed up for a few weeks. The steady-state

pressure of helium in the ampoule required to maintain a diffusion rate equal to the rate of production can be calculated from the dimensions of the capillary and the literature value of the diffusion constant through fused silica. Various determinations of the diffusion constant at 25° have given results varying from 0.11 to 0.06 cc at STP, mm $sec.^{-1}$ cm^{-2} $(cm\ Hg)^{-1}$[6]. By the formula $Q/t = 2\pi Dp/\ln(r_1/r_2)$, where Q/t is the quantity transported in unit time per cm length of capillary and D is the diffusion coefficient, and taking D = 0.08, we calculate for the steady-state pressure in ampoule 2 11 cm, and in ampoule 8 15 cm. The observed values are respectively 8.2 cm and 12 cm. Thus the escape of helium in this manner was to be expected, and provides a useful means of accurately estimating the activity contained within a silica tube. After a diffusion steady state has been reached, the rate of helium evolution should decrease gradually with time as the tritium decays. One of us is now engaged in obtaining an accurate value for the decay constant of tritium in this way, and the results should be available within a few months.

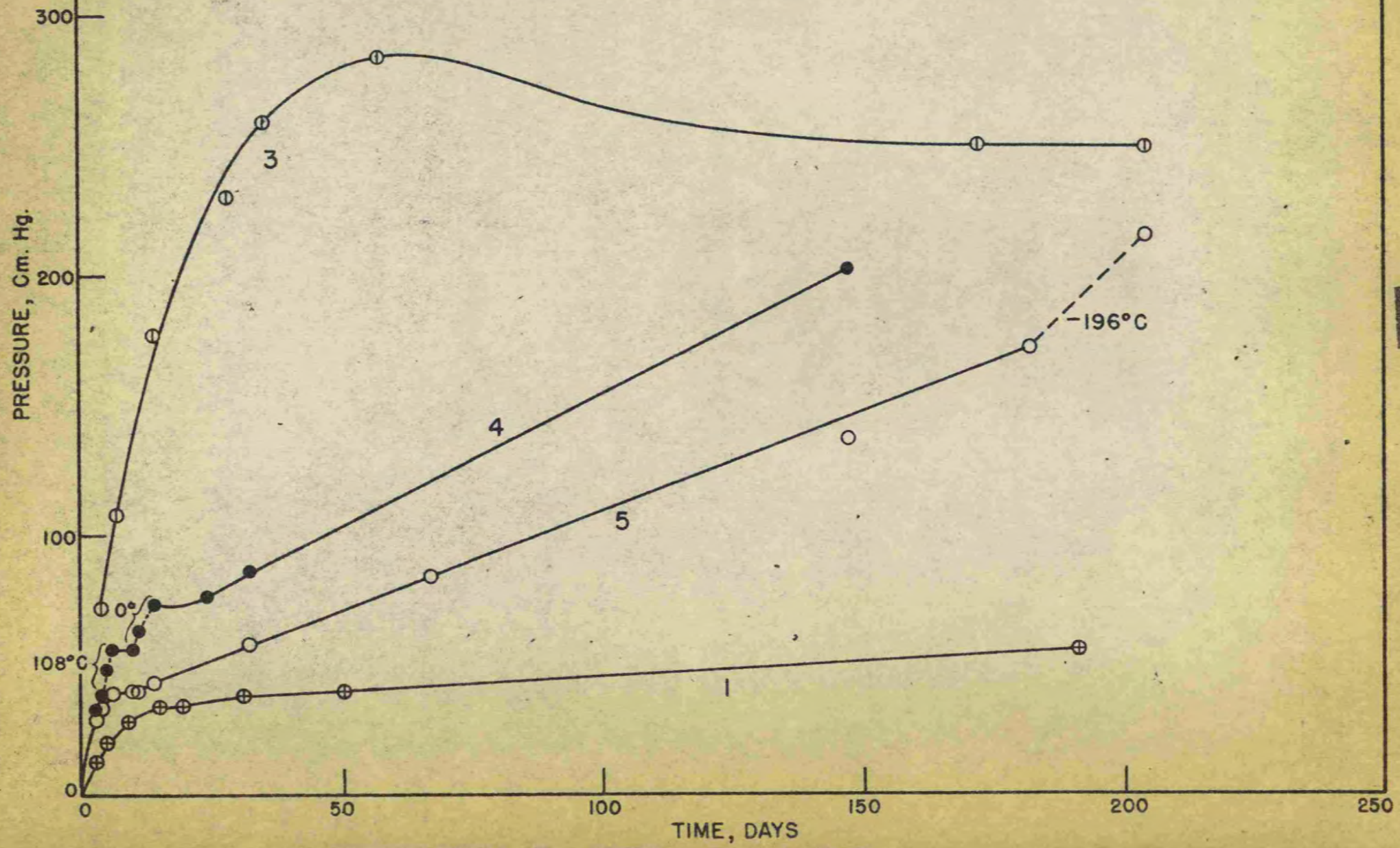
2. <u>The steady state pressure of electrolytic gas in the ampoules</u>. Curves of pressure versus time are shown for a number of the ampoules in Figures 1, 2 and 3. It is seen that the pressure rises rapidly at first; then the rise comes to a halt and a slight fall may even appear, and finally a period of relatively very slow pressure rise is reached. The initial rapid rise must be ascribed to the electrolytic gas formed by the decomposition of the water as a result of the tritium radiation. This rise is terminated when the steady state with respect to chemical decomposition of the water under this radiation has been reached. An exact value of this pressure cannot be determined, since some helium is also present, and it is difficult to calculate exactly how much of this helium has diffused out of the gas, since the steady state with respect to water decomposition is reached before the steady state with respect to helium diffusion. However, the maximum amount of helium that could be present is always considerably

Dwg. No. 5294

UNCLASSIFIED

FIG. 1

PRESSURE DEVELOPED IN WATER SAMPLES CONTAINING TRITIUM



UNCLASSIFIED

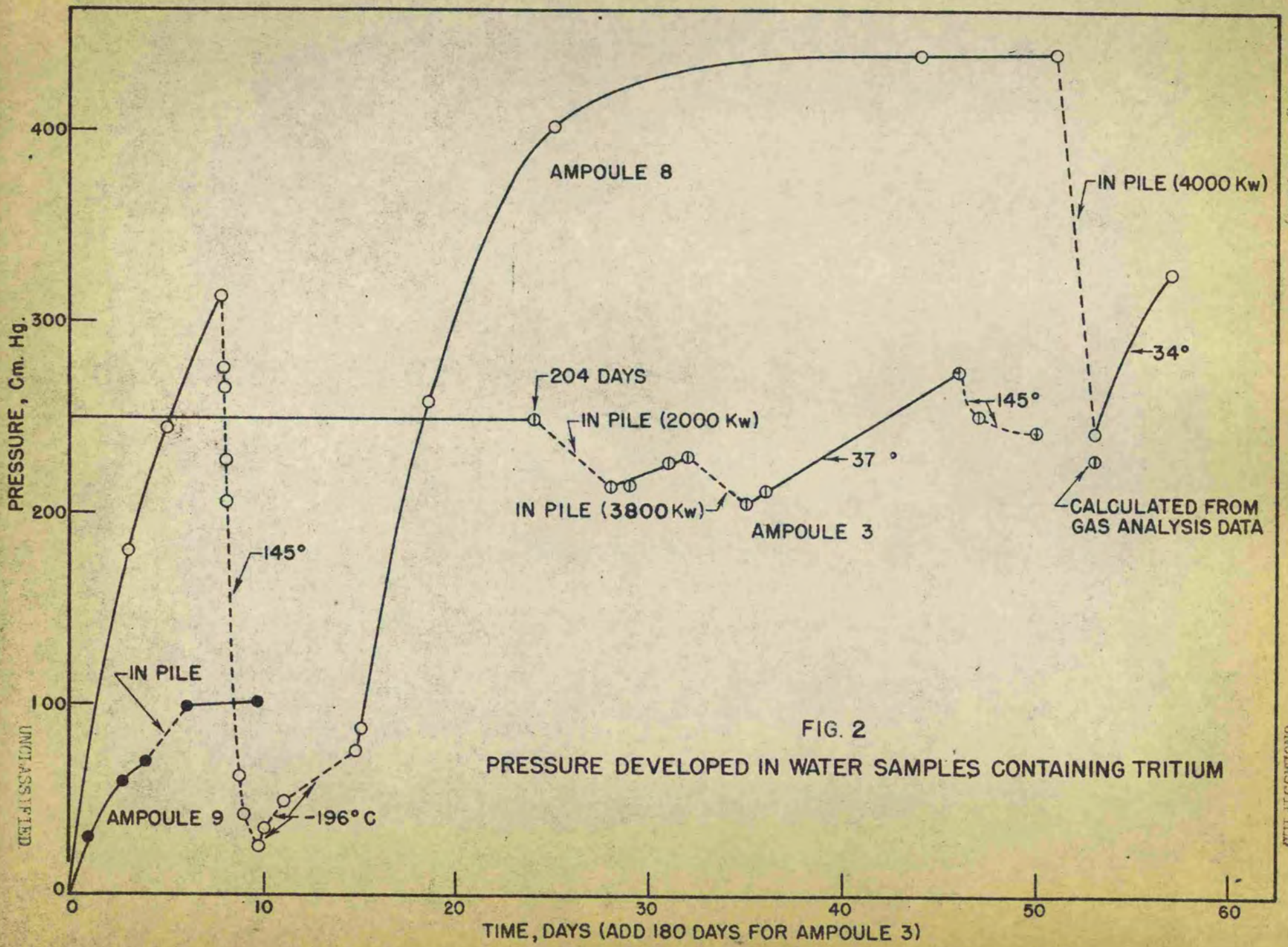


FIG. 2

PRESSURE DEVELOPED IN WATER SAMPLES CONTAINING TRITIUM

Dwg. No. 5264

UNCLASSIFIED

UNCLASSIFIED

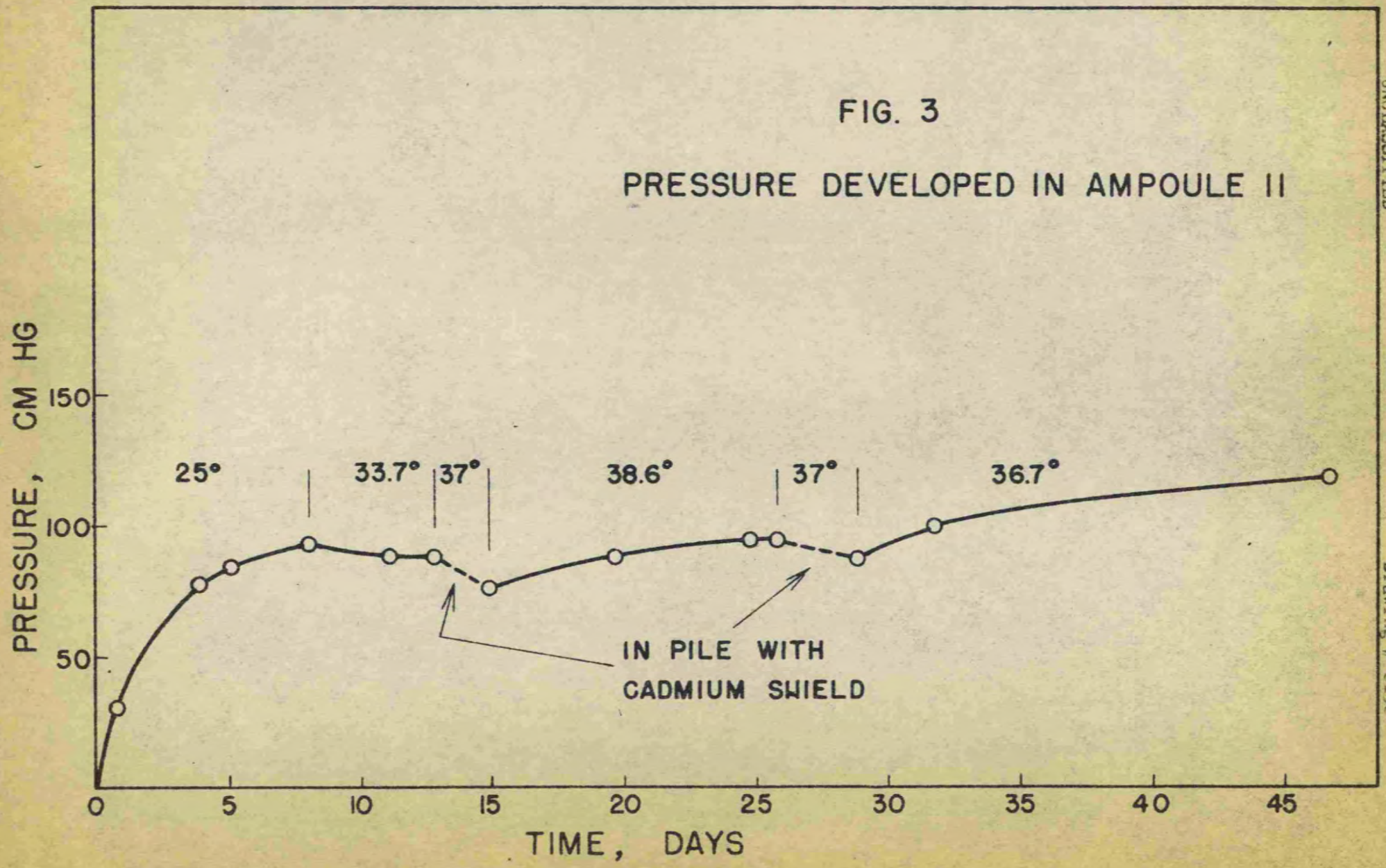


FIG. 3

PRESSURE DEVELOPED IN AMPOULE II

Drawing # 6136

less than the total pressure at these times. Estimates of the steady-state pressure of electrolytic gas could therefore be made with an accuracy of ± 10 cm or better. These estimates are shown in Table 1.

The steady-state pressures of electrolytic gas are found to vary tremendously from sample to sample, ranging from 20 cm for ampoule 5 to over 600 for ampoule 2 and apparently over 1300 for the lead-glass ampoule 7. The high pressure in the case of ampoules 2 and 3 is probably connected with the presence of copper impurity, since a small amount of copper ion was found to greatly increase the pressure obtainable over water under pile radiation[5]. In general, steady states are expected to be very sensitive to the presence of impurities which may react with free radicals liberated in the water by radiation and hence interrupt the radical-induced back reaction (which is almost certainly a chain reaction). Dissolved pyrex was found to increase the steady-state pressure in the case of irradiation by 1 Mev electrons;[3] and dissolved lead glass seems to exert a similar influence here. It is notable, however, that ampoules 9 and 11, in which the greatest pains were taken to obtain pure water, gave somewhat higher steady states than ampoules 1, 4 and 5. The water in number 1 was certainly contaminated with mercury and stopcock grease. It may be that the grease or some other impurity actually has the effect of reducing the steady-state level in radiation decomposition of water. Indications that organic impurities may act in this way were found in the study of the decomposition of heavy water under pile radiation[5]. We are certainly in no position to state what the steady-state level would be for a hypothetical "pure" water under radiation by tritium beta rays. It is noteworthy, however, that all the values found are far above the values of 1 or 2 cm pressure found in irradiation of water by 1 Mev electrons or X-rays. Thus, in this respect the expected difference in the behavior of water under electrons of widely differing energies has been demonstrated.

Table 1. Decomposition of tritium oxide sealed in ampoules

Ampoule Number	Ampoule Material	Method of Water Preparation	Activity, Curies	Method of Activity Determination	Gas Yield: Molecules per 100 ev	Gas Yield: Pressure range, cm Hg	Estimated Steady-state Pressure of Electrolytic Gas, cm Hg
1	Pyrex	HT + CuO	0.1	Ionization chamber			30
2	Silica	HT + CuO	0.9 ± .2	Same as No. 6	0.4	0 - 110	> 600
3	Silica	HT + CuO	0.60 ± .02	He^3	0.9 0.5	0 - 27 27 - 49	300
4	Silica	HT + O_2 (from K MnO_4)	1.1 ± .3	Estimated from 5			30
5	Silica	"	1.10 ± .02	He^3			20
6	Silica	Redistilled from No. 2	0.9 ± .2	Calorimeter	0.13	4 - 9	
7	Lead glass	Redistilled from No. 6	0.7 ± .2	Calorimeter			> 1600
8	Silica	Redistilled from No. 4	1.1 ± .3	Same water as No. 4			440
9	Silica	Fraction redistilled from No. 3	0.3 ± .1	Estimated from 3			80
10	Silica	Residue from preparation of No. 9	0.2 ± .1	Estimated from No.3			
11	Silica	Fraction redistilled from Nos. 8 and 10	0.77 ± .01	He^3			80

The maximum of pressure shown clearly in the case of ampoule 3 and the halt in the pressure rise indicated for ampoules 4 and 5, and suggested in the curve for ampoule 1, are probably to be ascribed to the complicated interaction between the peroxide and hydrogen contents of a solution at the steady state. The steady-state pressure of hydrogen under pile radiation has been shown to increase when the peroxide concentration is increased[5]. Peroxide thus not only is a reactant in the back reaction, but also, like many foreign substances, acts as an inhibitor for the back reaction. The decomposition of peroxide to oxygen always occurs under radiation, and may be expected to continue after a steady-state relation between the peroxide and hydrogen contents has been reached. By analogy with water exposed in the pile, we may assume that the peroxide concentration in the irradiated water here is considerably greater than the hydrogen concentration (since hydrogen mostly escapes into the gas phase as soon as formed, while peroxide remains in the water until it decomposes to oxygen). The excess peroxide will decrease the rate of back reaction and cause the hydrogen to build up to high levels. After a steady state has been reached with respect to hydrogen, the peroxide will continue to decompose slowly to oxygen, the oxygen will escape into the gas phase, the back reaction rate will increase, and the hydrogen pressure will fall. If the rate of the resulting fall in hydrogen pressure is greater than the rate of increase in oxygen pressure from peroxide decomposition, the total pressure will drop. This appears to be the case with ampoule number 3. After a time the peroxide-oxygen reaction will also come to a steady state and further changes in the hydrogen pressure will not occur at any noticeable rate. Such a hypothesis could, of course, be verified only by determination of the peroxide content of the water, which appeared impossible in the present case; the above explanation is based entirely on the known behavior of water and solutions exposed to pile radiation.

3. Slow accumulation of excess oxygen. As the tritium transmutes to helium in the water, a quantity of oxygen or peroxide equivalent to the hydrogen disappearing must build up in the system, over and above the oxygen produced by decomposition of the water (which should be equivalent to the hydrogen formed). After the steady states with respect to water decomposition and helium diffusion are reached, a slow rise in pressure follows, ascribed to this release of oxygen. Even if this oxygen is originally produced in the form of hydrogen peroxide (as seems likely), it will soon appear almost entirely in the gas phase as a result of the decomposition of the peroxide by radiation. The rate of this final slow pressure rise should therefore be equal to one-fourth of the rate of pressure rise which would be produced by accumulation of helium, if the helium did not diffuse out of the gas phase. In the case of ampoule 5, in which the tritium activity and volume of gas phase were both accurately known, the calculated rate of pressure rise due to oxygen was 3.72×10^{-4} atms./hr. while the observed rate of pressure rise after the first two weeks was 3.8×10^{-4} atmospheres per hour.

Gas analysis showed the presence of excess oxygen (see Table 2). For ampoules 2 and 3, the observed excess oxygen is somewhat greater than that calculated. This may be due to a diffusion of hydrogen into the walls of the ampoule, since the normal rate of diffusion of hydrogen through silica is only a few hundred times smaller than that of helium at room temperature; these ampoules contained high hydrogen pressures, and ampoule 3 before being opened had been exposed to pile radiation for many days and had been heated for four days at 145°. In the case of ampoule 6, the amounts of gas were small and a considerable part of the excess oxygen may have been tied up in the aqueous phase as hydrogen peroxide. For ampoule 8, the excess oxygen could be calculated only approximately, since tritium activity was not exactly known.

4. Initial rates. Since the rate of pressure rise falls off rapidly with time, a precise estimate of the initial rate of reaction is difficult. Another difficulty involved here is that the water must be generating gas during the

Table 2. Analysis of gas in tritium oxide ampoules.

Ampoule Number	Gas Volume, mm^3	Liquid Volume mm^3	Time, days	Gas Analysis H_2, mm^3 STP	O_2, mm^3 STP	He^3, mm^3 STP	Excess O_2 Observed, mm^3 STP	Calculated mm^3 STP
2	4.94	1.46	83	26.9	16.4	0.53	2.9	2.2
3	6.60	3.47	233	9.4	10.2	0.2	5.5	3.5
5	3.73	2.28						
6	2.31	1.44	11	1.19	0.74	0.39	0.14	0.29
8			150	13.4	12.5	0.74	5.8	
10	300		104	46.8	23.8	1.03		

entire process of filling and sealing the ampoule, during which the water may be frozen for as long as two hours; the proper time to take for the zero is consequently uncertain by about an hour or so. In Table 1, values of the rate of pressure rise between pressures shown are given in terms of molecules of gas formed per 100 ev of energy produced by beta radiation. The results suggest that about 1 molecule of gas is produced initially for 100 ev. This value is smaller than the yield of hydrogen produced by alpha radiation and greater than the value estimated for fast electrons, in agreement with the notion that radicals which escape by diffusion from the track of the radiation do not greatly contribute to the formation of decomposition products. An accurate idea of how many radicals are produced per 100 ev of this particular radiation could be obtained only by a study of the behavior of solutions. We have no explanation for the low rate shown by ampoule 6.

5. Temperature effect. An increase in temperature generally serves to reduce the steady state level in water decomposition, as shown in Figures 1, 2 and 3, but this effect was very different for different ampoules. Thus, in ampoule 8 the pressure dropped precipitately when the temperature of the ampoule was raised to 145°, while for ampoule 3 a small effect only was noticed. (Whenever no temperature is given in these Figures, the ampoule was maintained at 25°.) For ampoule 4, the rate of gas evolution was apparently increased by raising the temperature to 108°, and was also apparently increased by reducing the temperature to 0°. For ampoule 11, it is clear that an increase in temperature from 25° to 33.7° slightly lowered the steady-state pressure. The position of the steady state is determined by the reaction of the radicals with dissolved impurities, which apparently differ from ampoule to ampoule; and it seems that the temperature coefficient of the reaction is different for different kinds of impurity and therefore shows great variation as between the different ampoules.

6. Decomposition of ice. Many of the ampoules were cooled to liquid nitrogen temperature for considerable periods. This cooling was necessary for the calori-

metric determination of the activity. It was of interest to find out whether the decomposition of water to yield hydrogen under radiation continues in the solid state. At liquid nitrogen temperature, the rate of diffusion of helium through silica presumably becomes negligible, so that to determine the amount of electrolytic gas formed, one must subtract from the total measured pressure increase the total amount of helium formed during the low temperature period, together with the equivalent amount of excess oxygen produced as a result of the transmutation. Ampoule 8 was frozen for three different periods, with the gas pressure being measured before and after each period. Results of these measurements are shown in Table 3. It is clear that some gas was being formed by water decomposition during the low-temperature periods. The calculated amounts, given as "electrolytic gas" in the table, are lower limits, since some of the excess oxygen, which was assumed all to be in the gas phase, may have been tied up in the aqueous phase as hydrogen peroxide. The yield G (molecules of electrolytic gas per 100 ev) in this case is smaller the longer the exposure, indicating that back reaction may possibly occur in the solid phase as well as in the liquid. The pressure rise found during the low temperature period for ampoule 5 cannot be interpreted, since the ampoule was allowed to stand at room temperature for 18 hours before pressure measurement was made, and much helium may have diffused out of the gas phase into the glass wall during this time.

7. Effect of pile radiation. The best demonstration for the different effect of slow and fast electrons on the decomposition of water would be to irradiate with fast electrons a sample which had come to the steady state under tritium radiation, and note that a pressure drop occurred. Pile radiation contains a considerable hard gamma component which might be expected to act in this way. It was therefore of interest to place one of these tritium ampoules which had come to a steady state pressure in the pile and see whether the pressure fell. Such an experiment was tried with ampoule 3, and as shown in Figure 2 the

Table 3. Decomposition of ice in ampoule 8 at liquid nitrogen temperature

Time at -196°, hr.	Pressure increase, cm. Hg	Calculated electrolytic gas, cm. Hg	Electrolytic gas yield, G, molecules/100 ev
6.5	9	8	0.27
21.5	17	15	0.15
91.5	24	15	0.04

pressure did fall. In this experiment the ampoule was surrounded with an inch of water to minimize the amount of energy given up to the water by fast neutrons and thereby magnify the relative effect of the gamma rays. The total energy input to the water from pile radiation was of the same order of magnitude as that from the tritium radiation.

We could not be sure, however, that the back reaction found was actually occurring in the liquid phase. Helium^3 which is present in the gas undergoes an n,p reaction with thermal neutrons which is exothermic to the extent of 0.75 Mev and has a cross section of 6000 barns. We estimate, taking into account the geometry of the capillary, that this reaction will deliver about 5×10^{11} ev/sec. to the gas phase; the pile radiation alone would deliver less than 1% of this energy to the gas phase. It had been shown that the rate of recombination of hydrogen and oxygen in the gas phase in the pile was negligible(5), but we could not be sure that the n,p reaction would not increase the rate to the point where it became important. We, therefore, repeated the experiment with an ampoule shielded with cadmium to stop this n, p reaction. To demonstrate that the reaction really was reduced by the cadmium shield, a determination of the cadmium ratio for the reaction was made. Two samples of He^3, obtained by diffusion from an ampoule of tritium water, were sealed up and placed one above the other in Hole 12 of the pile. The samples contained the same amount of He^3 to within 10%. One was shielded with cadmium, the other unshielded. The insides of the ampoules were lined with palladium foil to catch all the tritium resulting from the n,p reaction. After the exposures the ampoules were opened under vacuum, the palladium heated in the presence of carrier hydrogen to extract the tritium, and activities of the resulting gas were measured in the ionization chamber. A second extraction from palladium was run to make sure that all activity was obtained. The activities found were in the ratio of 73:1 indicating that 98.7% of the reaction was cut out by the cadmium shield.

Ampoule 11 was prepared and allowed to come to a steady state at 33.7°, as shown in Figure 3. The ampoule was placed in the pile shielded by cadmium and water, and a definite drop in pressure was observed. The temperature of the water surrounding the ampoule was measured roughly and found to be 37°. Since the observed pressure drop in the pile could have been due to the higher temperature, the ampoule was allowed to come to a steady state outside the pile at 38.6°, and was again placed in the pile. A more careful measurement of the ampoule temperature by means of a thermocouple in contact with the water immediately surrounding the ampoule again indicated a temperature of 37°. As shown in Figure 3, another drop in pressure occurred while the ampoule was in the pile. When the temperature of the ampoule was maintained at 36.7° outside the pile, the pressure rose to a value consistent with the steady state found at 38.6°. Since the rate of pressure drop was approximately the same as found for ampoule 3 bombarded in the pile with no cadmium shield, it is evident that the observed pressure drop in ampoule 11 cannot be ascribed to back reaction in the gas produced by the effects of thermal neutrons. This is regarded as a good demonstration that fast electrons give a lower steady-state decomposition level of water than slowelectrons under the same conditions.

BIBLIOGRAPHY

(1) W. Duane and O. Scheuer, Le radium 10, 33 (1913); F. C. Lanning and S. C. Lind, J. Phys. Chem. 42, 1229 (1938).

(2) O. Risse, Z. physik. Chem. 140, 133 (1929); H. Fricke et al, J. Chem. Phys. 6, 229 (1938) and earlier papers.

(3) J. A. Ghormley, PPR Vol. 10B (to be published).

(4) A. O. Allen, J. Phys. Colloid Chem. 52, 479 (1948).

(5) Report ORNL-130.

(6) R. M. Barrer, "Diffusion in and through Solids", Cambridge University Press (1941).