

UNCLASSIFIED

AD 277 509

*Reproduced
by the*

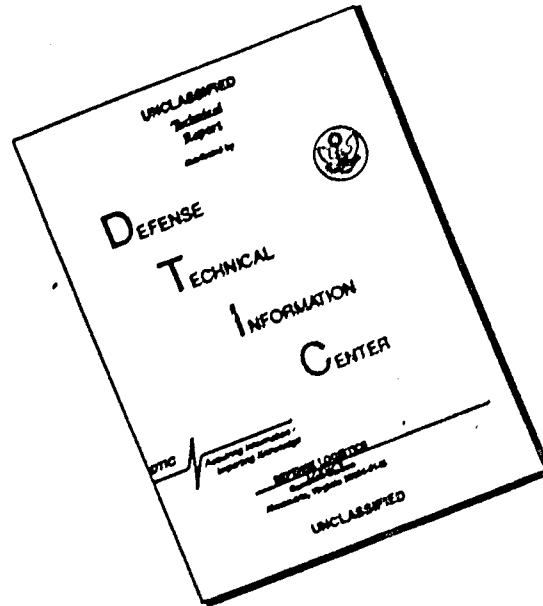
ARMED SERVICES TECHNICAL INFORMATION AGENCY
ARLINGTON HALL STATION
ARLINGTON 12, VIRGINIA



UNCLASSIFIED

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

DISCLAIMER NOTICE



THIS DOCUMENT IS BEST QUALITY AVAILABLE. THE COPY FURNISHED TO DTIC CONTAINED A SIGNIFICANT NUMBER OF PAGES WHICH DO NOT REPRODUCE LEGIBLY.

277 509

CONFIDENTIAL
277509

USNRDL-TR-565

Copy 94
8 May 1962

THE SELF-RADIATION OXIDATION OF
TRITIUM IN OXYGEN AND AIR

by
G. J. Casaletto
L. H. Gevantman
J. B. Nash

U. S. NAVAL RADIOLOGICAL
DEFENSE LABORATORY
SAN FRANCISCO 24, CALIFORNIA

APPLIED RESEARCH BRANCH
P. E. Zigman, Acting Head

CHEMICAL TECHNOLOGY DIVISION
L. H. Gevantman, Head

ADMINISTRATIVE INFORMATION

The work reported is part of a project sponsored by the Bureau of Ships under RDT&E Subproject No. S-F011 05 11, Task No. 0543. The project is described in this Laboratory's USNRDL Technical Program for Fiscal Years 1962 and 1963, Revised January 1962, where it is designated as Problem 5, Program D-1. Progress in the project is reported most recently in Quarterly Progress Report, 1 January to 31 March 1962, April 1962.

Eugene P. Cooper

Eugene P. Cooper
Scientific Director

E. B. Roth

E. B. Roth, CAPT USN
Commanding Officer and Director

ABSTRACT

The rate of self-radiation oxidation of tritium has been studied in atmospheres of oxygen and air by direct analysis of products as a function of time.

Second-order dependence on tritium concentration was observed below 1 mc/ml. Rate constants were determined to be 1.2×10^{-3} ml/mc-hr in oxygen and 0.62×10^{-3} ml/mc-hr in dry air.

The reaction rate was found to be independent of oxygen concentration and surface area at constant total pressures above 100 mm but to drop off sharply below this value.

The rate in oxygen is increased threefold in the presence of water vapor. The rate in atmospheric air, although poorly reproducible, is essentially the same as in dry air.

SUMMARY

The Problem

The radiation hazard to personnel from an accidental release of tritium gas increases with time because of the spontaneous conversion of tritium to tritium oxide. The latter is much more rapidly absorbed by the body because of its greater solubility. Knowledge of the rate of oxidation is necessary to permit a realistic evaluation of the danger at any time after such an accident.

The Findings

The rate of oxide production has been found to vary as the square of the tritium concentration in the region of practical interest, below 1 mc/ml. The observed rate in dry air is relatively slow, being only 1.5 % per day at the above concentration. Although the rate was found to be twice as great in pure oxygen and about six times as great in moisture-containing oxygen, the normal constituents of breathing atmospheres were not found to exert any large effect on the reaction rate.

INTRODUCTION

It has been shown by Pinson and Langham (Ref. 1) that the radiation health hazard presented by tritium oxide vapor in the atmosphere is at least 1000 times that presented by molecular tritium at equivalent concentrations because of the much more rapid absorption of the oxide into the body. Thus, initial estimates of the personnel hazard based on the often-used convention that all tritium is present as the oxide may be several orders of magnitude too high in the event of an accidental release of pure tritium gas. The concentration of oxide in the atmosphere does increase slowly with time after such a spill, however, since the tritium is oxidized in the atmosphere under the influence of its own β -radiation. Therefore, an accurate evaluation of the danger at any time after such a release can be made only if the rate of self-oxidation is known.

The oxidation of isotopes of hydrogen in the presence of various radiations has been the subject of a number of investigations, including an extensive series by Lind (Ref. 2) who studied the oxidation of hydrogen and deuterium in oxygen by irradiation with α -particles from radon. These and other studies of radiation chemical effects in gases also are discussed in a monograph by Lind (Ref. 3).

The self-oxidation of tritium in oxygen was studied by Dorfman and Hemmer (Ref. 4). The rate of reaction was followed by direct measurement of pressure change assuming T_2O as the end product, and was found to be directly proportional to tritium concentration and independent of oxygen concentration. A first-order rate constant of $1.19 \times 10^{-4} \text{ min}^{-1}$ was reported, corresponding to a half-life of 97 hr. This rate was observed over a concentration range between 94 and 324 millicuries/milliliter of tritium.

In the investigation described in this report it was desired to extend the existing knowledge of the self-oxidation rate of tritium to low initial tritium concentrations - conditions corresponding more nearly to an applied situation. Specific questions or problems to be examined were: Does the reported rate constant remain valid at concentrations of tritium below 1 mc/ml? What effects result from the introduction of nitrogen, water vapor, and other atmospheric constituents?

The direct exchange of tritium with water vapor has already been investigated by Yang and Gevantman (Ref. 5). The relation of this work to the oxidation studies was of particular interest as water vapor is invariably present in atmospheric air.

EXPERIMENTAL

Experimental Approach

Because of the low concentration of tritium to be studied (below 1 mm) it was not possible to follow the progress of the reaction by direct measurement of pressure change or other physical property. It was necessary to analyze the reaction mixture for condensable product formed at suitable time intervals. Methods were devised for separating unreacted tritium from the tritium oxide product, which was then determined by liquid scintillation counting. Details of the preparation and analysis of reaction mixtures are given in the following sections.

Apparatus and Procedure

Tritium-Dispensing System. Requirements for a suitable tritium-dispensing system were: storage away from air and stopcock grease; convenient withdrawal; maximum safety.

The pipetting system devised to meet these requirements is illustrated in Fig. 1. The pipette is basically a miniature Toepler pump calibrated for volume and provided with a manometer tube for simultaneous pressure measurement. A conventional break-seal ampoule containing the tritium is sealed into position, and the system is evacuated with the mercury lowered out of the manometer tube and pipette. The level is then raised to seal off the ampoule at the sintered disc, after which the break-seal is broken. Tritium gas now can be withdrawn by lowering the mercury level, the desired pressure and volume being read on the manometer and pipette. The sintered disc in the delivery line prevents mercury from being driven over accidentally. After each withdrawal, the supply ampoule is again sealed off with mercury at the sintered disc, preventing the tritium from remaining in contact with stopcock grease and minimizing the danger of a possible leak.

The tritium was purchased from the Oak Ridge National Laboratory, Oak Ridge, Tennessee in a purity of 99 % (min.) and used without further purification except for passage through a liquid-nitrogen-cooled U-tube before use.

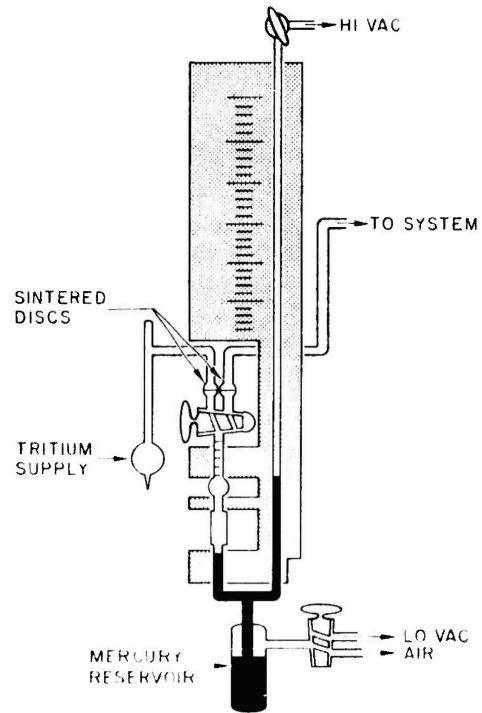


Fig. 1 Tritium-Metering Pipette

Gas-Handling Apparatus. Gas-handling apparatus used for these experiments were of conventional design. Vacuum was provided by a two-stage mercury diffusion pump with a Welch Duo Seal mechanical forepump. Pressures below 10^{-6} mm, read on a Veeco Type RG-2A ionization gauge, were reached under working conditions.

A small furnace containing a copper-oxide-filled tube was incorporated in the vacuum system and was kept at 450°C to allow excess gaseous tritium to be disposed of by conversion to the oxide which was frozen out in liquid nitrogen.

All stopcocks were lubricated with Apiezon N grease.

Tritium Counting. Suitable aliquots of the tritium oxide solutions to be analyzed were pipetted into 18 ml of a scintillant solution containing (per liter):

230 ml absolute ethanol
770 ml toluene
4 g 2,5 diphenyloxazole (PPO)
15 mg 1,4-bis-2 (5-phenyloxazolyl)-benzene (POPOP).

The scintillant solution was calibrated against National Bureau of Standards standard tritiated water and yielded counting efficiencies between 6 and 8 %. The counting was done on the Packard Tri-Carb liquid scintillation spectrometer.

Initial Experiments

Initial exploratory experiments were conducted in the apparatus illustrated in Fig. 2. Mixtures of tritium and air or oxygen were prepared in the single 1-ℓ reaction bulb. At suitable time intervals, small samples of the reaction mixture were withdrawn into one of the sampling bulbs. Unreacted tritium was separated from the tritium oxide product by freezing the latter in liquid nitrogen and pumping off the remaining gases. The residue was diluted and analyzed.

The results of these preliminary experiments gave strong evidence that the self-oxidation reaction at the concentrations studied was much slower than predicted from a simple extrapolation of the Dorfman and Hemmer data. The precision of the results was inadequate for quantitative rate determination, however, partly because of adsorption of tritium on the walls of the sampling manifold, which caused cross-contamination between samples. The withdrawal of samples from the main reaction vessel itself undoubtedly was affected by surface adsorption, so a revised method was used in subsequent experiments.

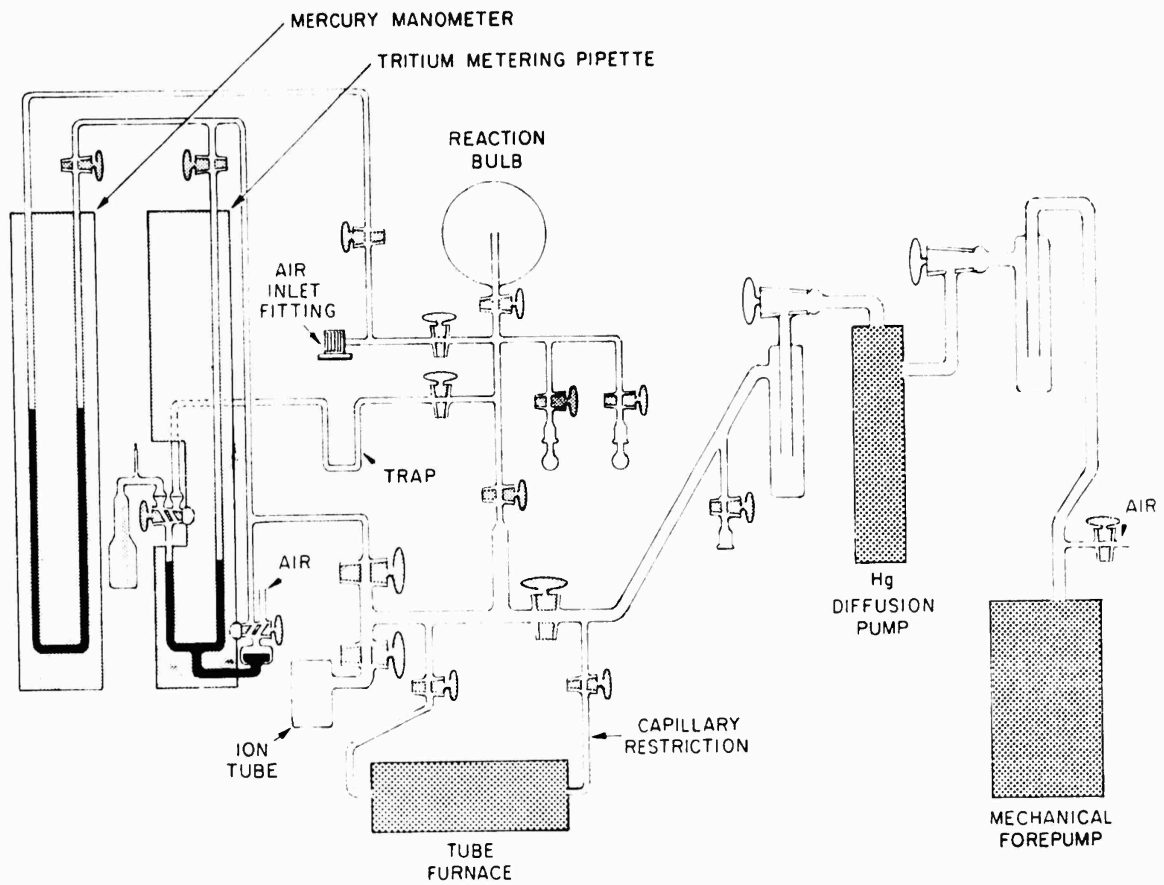


Fig. 2 Tritium-Handling System with Single Reaction Bulb

Revised Procedure

To eliminate the errors which seemed to be inherent in the "single bulb" method, a technique was employed which involved the simultaneous preparation of reaction mixtures in separate bulbs, five 250-ml bulbs being used for a single run. At appropriate time intervals, the contents of an entire bulb were taken for analysis. This procedure allowed the inner surface of the reaction vessel to be rinsed with water; thereby minimizing the effects of adsorption.

Before use, the reaction bulbs were boiled with nitric acid, rinsed, and pumped down to at least 10^{-6} mm. It was found that soaking in water for about 48 hr, followed by the above procedure, made them re-usable after a run. In the case of used bulbs, a preliminary boiling with benzene was found to be helpful in removing stopcock grease before the nitric acid treatment. During the pumping, the bulbs were not baked out since this made subsequent decontamination more difficult and, perhaps, interfered with the quantitative recovery of product.

The apparatus used is illustrated in Fig. 3. A typical run was started by measuring out the desired amount of tritium in the tritium pipette. The gas was then expanded through a liquid-nitrogen-cooled U-tube into the five previously evacuated bulbs. The amount of tritium in each bulb was calculated from the known volumes of the bulbs and manifold system. Oxygen, air, or other atmosphere was then added to complete the reaction mixture, and the bulbs were set aside to react at room temperature.

In the runs made to establish dependence on tritium concentration, the first bulb was usually sampled in about 2 hr, the remainder at intervals of 12 to 48 hr, depending on the expected rate. This scheme was varied in subsequent runs according to the parameter under study. In some cases, for example, it was desirable to vary the gas composition from one bulb to another and sample all the bulbs at once. The sampling procedure itself consisted of the following steps:

1. Add 15 ml water, shake 10 min.
2. Freeze 20 min in liquid nitrogen, pump down to 10^{-3} mm.
3. Thaw, add $1/2$ atm of hydrogen, shake 10 min.
4. Freeze 10 min, pump down to 5×10^{-5} mm.
5. Thaw, refreeze, pump to 1×10^{-6} mm.

The remaining water was then diluted by an appropriate factor and counted.

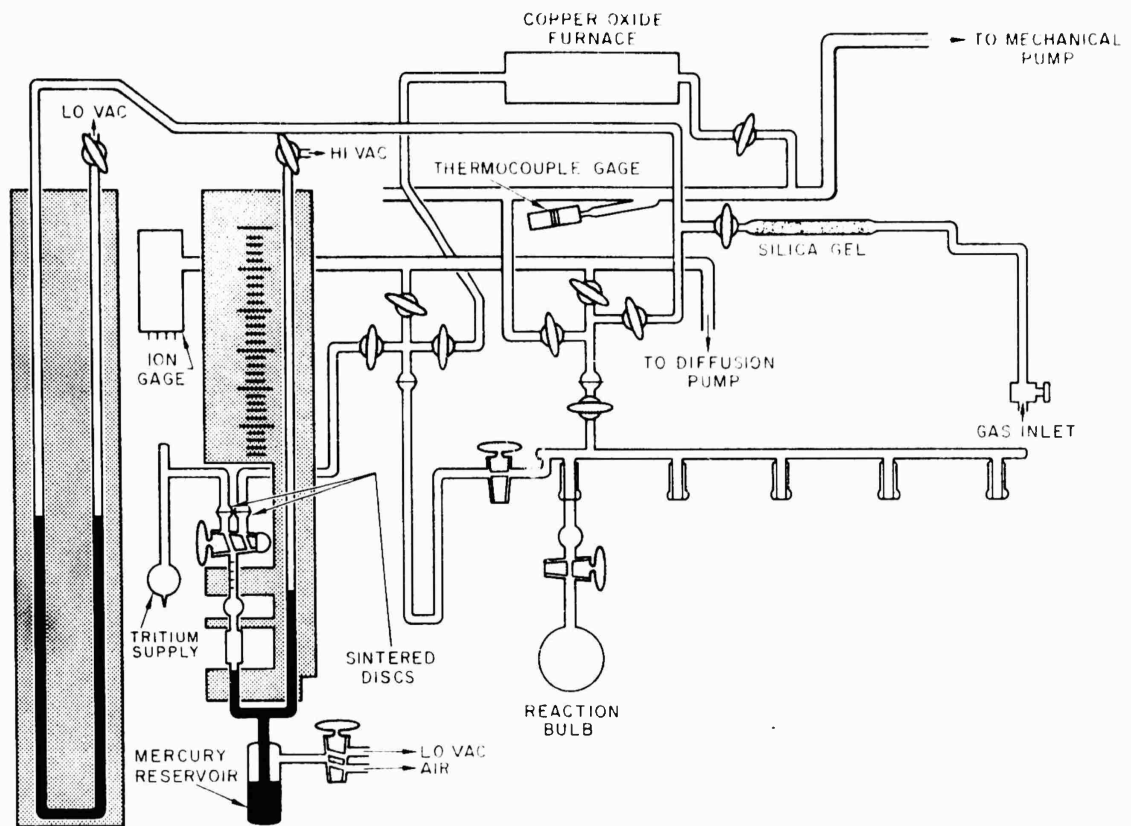


Fig. 3 Tritium-Handling System with Multiple Bulbs

Treatment of Data

The results of the analysis yielded amounts of tritium oxide formed as a function of time. These were converted to percent of reaction, using the initial concentration previously calculated. The total amount of reaction was kept below 5 %. Since the rate of reaction is nearly constant, regardless of order, over the first few percent, the conventional initial-rate approximation was made:

$$\text{slope} = - \frac{100}{(T_2)_0} \left[\frac{d(T_2)}{dt} \right]_0$$

where (T_2) is the tritium concentration and t is the time. The subscript "0" indicates initial conditions. Substitution into the differential form of the first order equation,

$$\text{Rate} = - \frac{d(T_2)}{dt} = k_1 (T_2),$$

allows the formal first-order rate constant, k_1 , to be calculated as:

$$k_1 = \frac{\text{slope}}{100} .$$

In the general case, k_1 may be found to be independent of reactant concentration, in which case the reaction is truly first-order; or a dependence of k_1 on one or more reactants may be found, in which case a more complicated situation would exist. In formulating a final rate expression, it is necessary also to distinguish between two cases: (a) where initial rate only is being described as a function of varying initial concentrations, and (b) where a general expression describing the behavior of the system over an extended run is being considered.

RESULTS AND DISCUSSION

Dependence on Tritium Concentration

The formal first-order rate constants, calculated as above, for the self-oxidation of tritium in oxygen and in air are shown in Fig. 4 as a

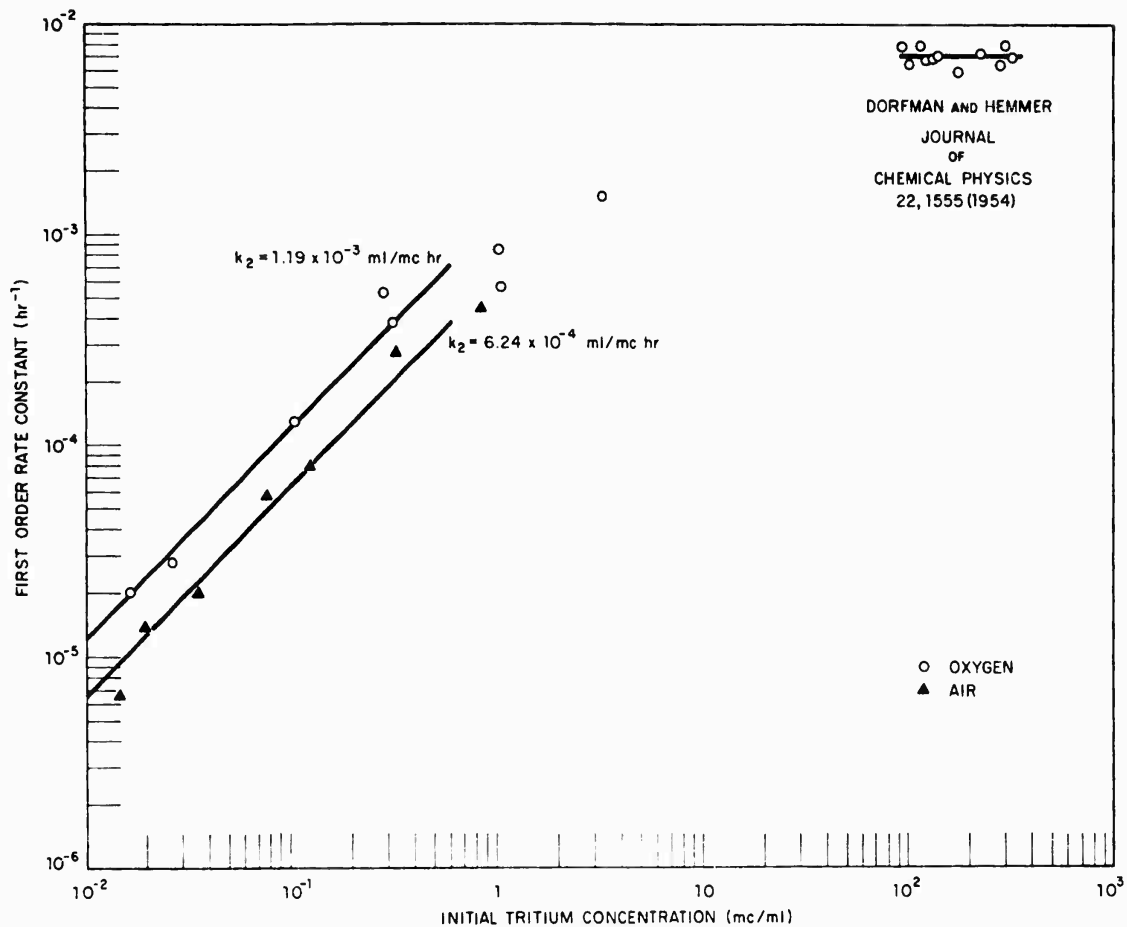


Fig. 4 Self-Radiation Oxidation Rate of Tritium

function of initial tritium concentration. Total pressure was 700 mm in all cases. The "constant" k_1 is seen itself to vary directly as the initial tritium concentration,

$$k_1 = k_2 (T_2)_0$$

where k_2 , the second order constant, is a true constant. Thus the correct expression for the initial rate is

$$R_0 = \left[- \frac{d(T_2)}{dt} \right]_0 = k_2 (T_2)_0^2.$$

An expression is needed for the rate of an individual run over an extended period of time. The most simple equation which might be proposed would be of the form:

$$R = - \frac{d(T_2)}{dt} = k_2 (T_2)_0 (T_2),$$

where one of the tritium terms remains as initial concentration because it simply represents the radiation intensity and ~~this~~ is not consumed in the normal sense during the reaction. This equation has not been verified in the case of the oxidation reaction, but has given a good fit in the case of water exchange (Ref. 6).

The experimentally observed second-order rate constant with oxygen is 1.2×10^{-3} ml/mc hr; with dry air it is 0.62×10^{-3} ml/mc hr.

The results obtained by Dorfman and Hemmer (Ref. 4) are also included in Fig. 4, and it may be observed that our results can be extrapolated to meet theirs. The extrapolation would involve a rather abrupt transition from second to first order. It seems more likely that the Dorfman and Hemmer points are actually in an intermediate region, the upward slope of the curve being masked by experimental error.

Dependence on Oxygen Concentration

The decreased reaction rate in air suggests the possibility of a dependence of the rate on oxygen concentration. This possibility was investigated by studying the rate under varying oxygen concentrations.

The results of a typical run are given in Table 1. The reaction mixtures were all brought up to 700 mm with nitrogen to be sure that essentially all the β -particles from the tritium were absorbed in the gas phase. There is no obvious trend in the rates, and the average compares well with the results predicted from Fig. 4, for a tritium concentration of 0.259 mc/ml in an air atmosphere. It is concluded that the reaction is independent of oxygen concentration as such and that the decreased rate in air is due to the behavior of the nitrogen itself.

TABLE 1

Effect of Variation of Oxygen Pressure on the Self-Oxidation of Tritium. (Initial Tritium: 0.259 mc/ml; Diluent: Tank Nitrogen; Total Pressure: 700 mm.)

Sample No.	Oxygen (mm)	Time (hr)	Percent Reaction	k_1
1	0.0	145.5	2.96	$2.03 \times 10^{-4} \text{ hr}^{-1}$
3	6.2	146.3	2.38	1.63
4	44.8	146.8	2.99	2.04
5	123.8	145.7	2.12	1.46
6	348.8	146.2	3.30	2.26
Average:				$1.88 \times 10^{-4} \text{ hr}^{-1}$

It is seen from Table 1 that the rate was undiminished even when no oxygen was intentionally added. Since some oxygen undoubtedly was present in the tank nitrogen, this point was further investigated by studying the behavior of tritium diluted with (a) reagent grade helium, and (b) commercial helium purified by being passed through a charcoal column at liquid nitrogen temperature. Helium was used instead of nitrogen because it is more easily purified and to eliminate the possibility of a reaction between tritium and nitrogen. Again, there was no decrease in the rate. The tritium evidently is capable of reacting with extremely small concentrations of oxidant. It must be pointed out that stoichiometry is easily accounted for, since under the conditions of these experiments, 0.005 % of oxygen in the inert gas is sufficient to give the observed results. The implications of this observation with respect to mechanism will be discussed in more detail in a later section.

Oxidation in the Presence of Water

Since water vapor is invariably present in atmospheric air it is important to establish the relation between the self-oxidation and water exchange reactions under conditions where both may occur simultaneously. The second-order rate constant, 1.7×10^{-3} ml/mc hr, reported by Yang and Gevantman, for the water exchange reaction is close to the value 1.2×10^{-3} ml/mc hr reported here for the self-oxidation in oxygen. This agreement, as well as the persistence of the oxidation reaction in the purest available inert gases, led to the possibility that in the preceding studies the two reactions were actually taking place simultaneously or even that they might be identical. Because of this question it was necessary to study the oxidation and water exchange reactions, each under such conditions that the other was least likely to interfere.

To eliminate water as completely as possible from the tritium-oxygen reaction mixtures, the latter were prepared in bulbs of fused quartz which had previously been baked for 4 hr at 10^{-6} mm and 500°C . The product was recovered in the normal manner and the rate corresponded exactly with that measured in unbaked Pyrex bulbs.

Because of the difficulty previously noted in preparing completely oxygen-free inert gases, the water exchange reaction was re-examined in the presence of water vapor alone (Ref. 6). To obtain a vapor pressure high enough to insure that essentially all the tritium β -energy was absorbed in the gas phase, the reaction was run at 85°C and enough water was added to give 400 mm pressure. This procedure was justified by the observation of Schiflett and Lind (Ref. 7) that the radiation chemical oxidation of hydrogen has a very small temperature coefficient in this temperature region. The water used was degassed thoroughly and the bulbs were sealed to eliminate stopcocks. A blank containing only tritium was included in the series to check the possibility of oxidation being caused by the sealing-off operation. None was observed. The exchange rate measured under these conditions duplicated that of Yang and Gevantman satisfactorily.

The above results indicate that the oxidation and water exchange reactions proceed independently of each other and are in fact distinct, the similarity in the rates being due to similar rate-determining steps in their respective mechanisms. The possibility of complications arising when tritium reacts with an atmosphere containing water and oxygen thus made it desirable to study this reaction directly.

Mixtures of tritium, water, and oxygen were first prepared in Pyrex bulbs using the multiple bulbs technique. A rate approximately twice

that in dry oxygen was measured, but precision was not satisfactory. The experiment was repeated by Smith (Ref. 6) using the single bulb procedure of Yang and Gevantman. A second-order rate constant of 4.3×10^{-3} ml/mc hr was obtained. This is approximately three times the rate of self-oxidation in dry oxygen.

Oxidation in Atmospheric Air

Because of the demonstrated acceleration of the self-oxidation reaction in atmospheres containing both oxygen and water, it was considered desirable to study the conversion of tritium to tritium oxide in actual breathing atmospheres, in case other minor components might also influence the reaction rate. Samples of breathing atmospheres were taken from spaces typical of those where tritium contamination might occur. Mixtures of tritium and these samples were studied through the same techniques as in the case of oxygen or dry air. There was a marked scatter in the results as might be expected from the many constituents undoubtedly present in the atmospheric samples, and it was not possible to derive precise rate constants. It was determined, however, that the rate of self-oxidation was approximately the same as in dry air. Although these gases did contain moisture, the similarity to dry air is possibly due to a compensating effect of substances which might act as inhibitors.

Further Experiments

Additional experiments were conducted in an effort to provide the basis for a coherent mechanism correlating the above observations.

The effect of surface area was studied by carrying out the reaction of tritium and oxygen in bulbs whose surface area was increased. Two bulbs of 500-ml capacity were indented over their entire surface to give a threefold increase in surface-to-volume ratio. Comparison with the results of a reaction run in an unindented 500-ml bulb showed no significant effect due to the increased surface.

The effect of change in total pressure was studied by preparing mixtures of tritium and oxygen containing oxygen at pressures between 5 and 700 mm without an inert gas diluent. A bulb containing tritium alone was included in the series as a blank. At 100 mm pressure and above, the rate was essentially constant; at 20 mm the rate was reduced to 10 % of the maximum value; and at 5 mm it was reduced to 0.5 %, which was the same as the background observed in the blank.

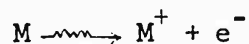
The β -energy absorbed by tritiated gases in spherical vessels as a function of vessel size and absorption coefficient of the gas has

been calculated by Meuller (Ref. 8). According to these calculations, the energy absorbed in oxygen at 20 and 5 mm is 55 and 21 %, respectively, of the total. Our observation of a considerably more rapid drop-off in the rate with decreasing pressure indicates that the effect is not due entirely to the decrease in absorbed energy. An inhibiting action, such as chain termination at the walls of the container, is indicated.

Mechanism

Although it is difficult to formulate an over-all mechanism to correlate the experimental observations, it is possible to interpret the latter in terms of some of the elementary steps proposed for radiation-induced reactions.

It is consistent with all available evidence to assume that the primary step in the self-oxidation reaction is ionization of the gases by the tritium β -radiation. In the presence of a large excess of inert gas, M, the principal process must be



Possibilities such as radiolysis of the surface or surface-bound materials are eliminated by the observed independence of surface area and the drop-off in rate at low pressures. The agreement between previous investigations using tritium (Ref. 4) and α -particles (Ref. 2), as an ionization source, also eliminates the possibility of a large contribution from chain reactions initiated by the tritium atom (more precisely $\text{He}^3 \text{T}^+$) formed in the decay process.

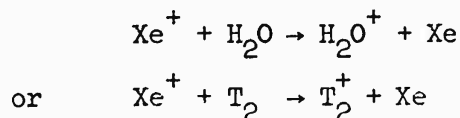
It has been demonstrated previously (Ref. 9) that ionization of an inert gas molecule can be as effective in promoting a radiation-chemical reaction as the ionization of a reactant. This necessitates some form of energy transfer between the inert gas ion and the reactant. In the present case, the reaction is observed to be second-order in tritium and zero-order in oxygen. This implies that the energy is transferred to tritium, not to oxygen. If one assumes that essentially every tritium molecule so activated eventually reacts with some oxidant, it is easy to explain the similarity in the rates for oxidation and water exchange.

It has been observed that xenon is almost as effective as the other inert gases in bringing about the radiation-induced oxidation of hydrogen (Ref. 9) and the self-induced water exchange by tritium (Ref. 6).

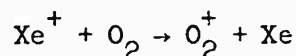
The ionization potentials of the molecules concerned are as follows (Ref. 3):

Xe	12.13 eV
H ₂	15.43
O ₂	12.10
H ₂ O	12.62

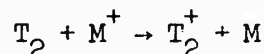
Since the ionization potential of xenon is below that of hydrogen or water, a simple charge transfer mechanism



cannot take place. In the oxidation reaction, the process

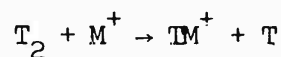


is possible, although charge transfer to tritium, which seems to be the more reasonable course, is not. We conclude that the energy transfer process is not a simple charge transfer:



The process has been explained by Lind on the basis of a clustering mechanism in which the inert gas ion surrounds itself with reactant molecules - a process somewhat analogous to the solvation of an ion in solution.

Eyring has pointed out that an inert gas ion should display the characteristics of an extremely reactive halogen atom (Ref. 10). It would then be possible for reactions to occur such as



leading to the ultimate products.

It is necessary to clarify further the observed total independence of oxygen concentration. Lind has shown (Ref. 11) that if a radiation-chemical oxidation reaction is possible in a given system, oxidation occurs to the exclusion of any other reaction. This behavior was attributed to the affinity of oxygen for free electrons which is so great

that all the free electrons ultimately form O_2^- . Lind stated that neutralization of the positive clusters preceded the formation of stable products. Since all the free electrons are present as O_2^- , the neutralization process must lead to oxide formation.

It must be noted that the supply of O_2^- is dependent on the number of free electrons available, that is, on the number of ionization processes taking place, and not on the oxygen concentration. If one agrees that neutralization of the positive ions precedes the formation of stable products, then the reaction is with O_2^- and not with O_2 , hence independent of the O_2 concentration.

CONCLUSIONS AND RECOMMENDATIONS

The self-oxidation of tritium has been shown to follow a second-order rate law:

$$\text{Rate}_o = k_2 (T_2)_o^2$$

or $\text{Rate} = k_2 (T_2)_o (T_2)$

where

$$k_2 = 1.2 \times 10^{-3} \text{ ml/mc hr in oxygen and} \\ 0.62 \times 10^{-3} \text{ ml/mc hr in dry air.}$$

The rate is independent of oxygen concentration and surface area at constant total pressures above 100 mm, but drops off rapidly at lower pressures.

The rate in oxygen is increased by a factor of approximately three by the presence of water vapor; the rate in ordinary atmospheric air tends to be irreproducible but is generally the same as in the case of dry air.

The observed independence of surface area does not preclude the occurrence of all surface effects especially in the case of metallic or oxidized surfaces. These effects will be the subject of a future investigation.

The relation between the water exchange and oxidation reactions also merits further study. It would be of particular interest to devise methods for distinguishing between T_2O and HTO in the condensible products and between T_2 and HT in the non-condensable gases.

REFERENCES

1. E. A. Pinson, W. H. Langham. Physiology and Toxicology of Tritium in Man. J. Appl. Physiol. 10:108 (1957).
2. S. C. Lind and others. Chemical Action Produced by Radon, Parts I Through V. J. Am. Chem. Soc. 41:531, 551 (1919); 45:2585, 2593 (1923); 46:2003 (1924).
3. S. C. Lind. Radiation Chemistry of Gases. Reinhold Publishing Corp., New York, 1961.
4. L. M. Dorfman, B. A. Hemmer. Ion-Pair Yield of the Tritium-Oxygen Reaction. J. Chem. Phys. 22:1555 (1954).
5. J. Y. Yang, L. H. Gevantman. Tritium β Radiation-Induced Isotopic Exchange in the T_2 - H_2O System. U. S. Naval Radiological Defense Laboratory Technical Report, USNRDL-TR-471, 28 Sept. 1960.
6. C. H. Smith, G. J. Casaletto, L. H. Gevantman. The Effect of Various Gases on the Self-Induced Isotopic Exchange Between Tritium and Water Vapor. U. S. Naval Radiological Defense Laboratory Technical Report in preparation.
7. C. H. Schiflett, S. C. Lind. The Temperature Coefficient of the Rate of Combination of Hydrogen and Oxygen Under Alpha Radiation. J. Phys. Chem. 38:327 (1934).
8. M. M. Mueller. A Calculation of the Beta Energy Absorbed by Tritiated Gases in Spherical Vessels. Los Alamos Scientific Laboratory Report LAMS-2580, 22 May 1960.
9. S. C. Lind, D. C. Bardwell. Chemical Action of Gaseous Ions Produced by Alpha Particles, VIII. The Catalytic Influence of Ions of Inert Gases. J. Am. Chem. Soc. 48:1575 (1926).

10. S. C. Lind. Chemical Activation by Gaseous Ionization. J. Chem. Phys. 7:790 (1939).
11. S. C. Lind, D. C. Bardwell. The Chemical Action of Gaseous Ions Produced by Alpha Particles VI. Reactions of the Oxides of Carbon. J. Am. Chem. Soc. 47:2675 (1925).

DISTRIBUTION

CopiesNAVY

1-3 Chief, Bureau of Ships (Code 335)
 4 Chief, Bureau of Ships (Code 320)
 5 Chief, Bureau of Ships (Code 603w)
 6 Chief, Bureau of Ships (Code 665)
 7 Chief, Bureau of Naval Weapons (RRMA-11)
 8-9 Chief, Bureau of Yards and Docks (Code 74)
 10 Chief, Bureau of Yards and Docks (Code E-400)
 11 Chief of Naval Operations (Op-07T)
 12 Chief of Naval Research (Code 104)
 13 Special Projects Officer
 14-16 Director, Naval Research Laboratory (Code 2021)
 17 Office of Naval Research (Code 422)
 18-23 Office of Naval Research, FPO, New York
 24 Naval Medical Research Institute
 25 U.S. Naval Hospital, San Diego
 26 U.S. Naval Postgraduate School, Monterey
 27 Office of Patent Counsel, San Diego

ARMY

28 Chief of Research and Development (Atomic Division)
 29 Chief of Research and Development (Life Science Division)
 30 Chief of Engineers (ENGM-C-EB)
 31 Chief of Engineers (ENGM-C-DE)
 32 Chief of Engineers (ENGRD-S)
 33 CG, Ballistic Research Laboratories
 34 Chief Chemical Officer (Director for Safety)
 35 CG, Chemical Corps Res. and Dev. Command
 36 Hq, Chemical Corps Materiel Command
 37 President, Chemical Corps Board
 38 CO, Chemical Corps Training Command
 39 Commandant, Chemical Corps Schools (Library)
 40 CO, Chemical Research and Development Laboratories
 41 Commander, Chemical Corps Nuclear Defense Laboratory
 42 Hq, Army Environmental Hygiene Agency
 43 CG, Aberdeen Proving Ground
 44 CO, Army Medical Research Laboratory
 45 Director, Walter Reed Army Medical Center

46 CG, Quartermaster Res. and Eng. Command
 47 Quartermaster Food and Container Institute
 48 Hq, Dugway Proving Ground
 49-51 The Surgeon General (MEDNE)
 52 CG, Engineer Res. and Dev. Laboratory
 53 Director, Office of Special Weapons Development
 54 CO, Office of Ordnance Research
 55 CO, Watertown Arsenal
 56 CG, Ordnance Tank-Automotive Command
 57 CO, Ordnance Materials Research Office, Watertown
 58 CO, Picatinny Arsenal
 59 CO, Frankford Arsenal
 60 CG, Army Ordnance Missile Command

AIR FORCE

61 Assistant Chief of Staff, Intelligence (AFCIN-3B)
 62-67 Commander, Aeronautical Systems Division (ASAPRD-NS)
 68 Directorate of Civil Engineering (AFOCE-ES)
 69 Director, USAF Project RAND
 70-71 Commandant, School of Aerospace Medicine, Brooks AFB
 72 Office of the Surgeon (SUP3.1), Strategic Air Command
 73 Office of the Surgeon General
 74 Commander, Special Weapons Center, Kirtland AFB
 75 Director, Air University Library, Maxwell AFB
 76-77 Commander, Technical Training Wing, 3415th TTG
 78 Commander, Electronic Systems Division (CRZT)

OTHER DOD ACTIVITIES

79-81 Chief, Defense Atomic Support Agency (Library)
 82 Commander, FC/DASA, Sandia Base (FCDV)
 83 Commander, FC/DASA, Sandia Base (FCTG5, Library)
 84 Commander, FC/DASA, Sandia Base (FCWT)
 85-94 Armed Services Technical Information Agency
 95 Director, Armed Forces Radiobiology Research Institute

OCDM

96 Office of Civil Defense, Battle Creek
 97 Office of Civil Defense, Washington

AEC ACTIVITIES AND OTHERS

98 Research Analysis Corporation
 99 Aerojet-General, Azusa
 100 Aerojet-General, San Ramon
 101 Allis-Chalmers Manufacturing Co., Milwaukee
 102 Allis-Chalmers Manufacturing Co., Washington
 103 Allison Division - GMC
 104-105 Argonne Cancer Research Hospital
 106-115 Argonne National Laboratory

116	Atomic Bomb Casualty Commission
117	AEC Scientific Representative, France
118	AEC Scientific Representative, Japan
119-121	Atomic Energy Commission, Washington
122-125	Atomic Energy of Canada, Limited
126-129	Atomics International
130-131	Babcock and Wilcox Company
132-133	Battelle Memorial Institute
134	Beryllium Corporation
135-138	Brookhaven National Laboratory
139	Bureau of Mines, Albany
140	Bureau of Mines, Salt Lake City
141	Chance Vought Aircraft, Inc.
142	Chicago Patent Group
143	Columbia University (Cropper)
144	Combustion Engineering, Inc.
145	Combustion Engineering, Inc. (NRD)
146	Committee on the Effects of Atomic Radiation
147-148	Convair Division, Fort Worth
149	Defence Research Member
150	Denver Research Institute
151	Division of Raw Materials, Washington
152	Dow Chemical Company, Rocky Flats
153-155	duPont Company, Aiken
156	duPont Company, Wilmington
157	Edgerton, Germeshausen and Grier, Inc., Goleta
158	Edgerton, Germeshausen and Grier, Inc., Las Vegas
159	General Atomic Division
160-161	General Electric Company (ANPD)
162-165	General Electric Company, Richland
166	General Electric Company, St. Petersburg
167	Glasstone, Samuel
168-169	Goodyear Atomic Corporation
170	Grand Junction Office
171	Hawaii Marine Laboratory
172	Hughes Aircraft Company, Culver City
173-174	Iowa State University
175	Jet Propulsion Laboratory
176-177	Knolls Atomic Power Laboratory
178	Lockheed Aircraft Corporation
179-180	Los Alamos Scientific Laboratory (Library)
181	Mallinckrodt Chemical Works
182	Maritime Administration
183	Martin Company
184	Massachusetts Institute of Technology (Hardy)
185	Monsanto Chemical Company
186	Mound Laboratory
187	NASA, Lewis Research Center
188	National Bureau of Standards (Library)
189	National Bureau of Standards (Taylor)
190	National Lead Company of Ohio
191	New Brunswick Area Office

192 New York Operations Office
 193 Nuclear Materials and Equipment Corporation
 194 Nuclear Metals, Inc.
 195 Oak Ridge Institute of Nuclear Studies
 196 Patent Branch, Washington
 197-200 Phillips Petroleum Company
 201 Power Reactor Development Company
 202-205 Pratt and Whitney Aircraft Division
 206 Princeton University (White)
 207-208 Public Health Service, Washington
 209 Public Health Service, Las Vegas
 210 Public Health Service, Montgomery
 211 Purdue University
 212 Radiation Applications, Inc.
 213 Sandia Corporation, Albuquerque
 214 Sandia Corporation, Livermore
 215 Sylvania Electric Products, Inc.
 216 Technical Research Group
 217-219 Union Carbide Nuclear Company (ORGDP)
 220-223 Union Carbide Nuclear Company (ORNL)
 224 Union Carbide Nuclear Company (Paducah Plant)
 225 United Nuclear Corporation (NDA)
 226 U.S. Geological Survey, Denver
 227 U.S. Geological Survey, Menlo Park
 228 U.S. Geological Survey, Naval Gun Factory
 229 U.S. Geological Survey, Washington
 230 U.S. Geological Survey, WR Division, Washington
 231-232 University of California Lawrence Radiation Lab., Berkeley
 233-234 University of California Lawrence Radiation Lab., Livermore
 235 University of California, Los Angeles
 236 University of Puerto Rico
 237 University of Rochester (Atomic Energy Project)
 238 University of Utah
 239 University of Washington (Donaldson)
 240-241 Westinghouse Bettis Atomic Power Laboratory
 242 Westinghouse Electric Corporation
 243 Yankee Atomic Electric Company
 244-268 Technical Information Service, Oak Ridge

USNRDL

269-310 USNRDL, Technical Information Division

DISTRIBUTION DATE: 9 July 1962

<p>Naval Radiological Defense Laboratory USNRDL-TR-565</p> <p>THE SELF-RADIATION OXIDATION OF TRITIUM IN OXYGEN AND AIR by G.J. Casaletto, L.H. Gevantman, and J.B. Nash 8 May 1962 25 p. table illus. 11 refs. UNCLASSIFIED</p> <p>The rate of self-radiation oxidation of tritium has been studied in atmospheres of oxygen and air by direct analysis of products as a function of time.</p> <p>Second-order dependence on tritium concentration was observed below 1 mc/ml. Rate constants were determined to be 1.2×10^{-3} ml/mc-hr in</p> <p>(over)</p>	<ol style="list-style-type: none"> 1. Tritium - Radioactivity. 2. Tritium oxide. 3. Water - Exchange reactions. 4. Water vapor - Chemical reaction. 5. Air - Radioactivation analysis. <ol style="list-style-type: none"> I. Casaletto, G.J. II. Gevantman, L.H. III. Nash, J.B. IV. Title. V. S-F011 05 11. <p>UNCLASSIFIED</p>
<p>Naval Radiological Defense Laboratory USNRDL-TR-565</p> <p>THE SELF-RADIATION OXIDATION OF TRITIUM IN OXYGEN AND AIR by G.J. Casaletto, L.H. Gevantman, and J.B. Nash 8 May 1962 25 p. table illus. 11 refs. UNCLASSIFIED</p> <p>The rate of self-radiation oxidation of tritium has been studied in atmospheres of oxygen and air by direct analysis of products as a function of time.</p> <p>Second-order dependence on tritium concentration was observed below 1 mc/ml. Rate constants were determined to be 1.2×10^{-3} ml/mc-hr in</p> <p>(over)</p>	<ol style="list-style-type: none"> 1. Tritium - Radioactivity. 2. Tritium oxide. 3. Water - Exchange reactions. 4. Water vapor - Chemical reaction. 5. Air - Radioactivation analysis. <ol style="list-style-type: none"> I. Casaletto, G.J. II. Gevantman, L.H. III. Nash, J.B. IV. Title. V. S-F011 05 11. <p>UNCLASSIFIED</p>

oxygen and 0.62×10^{-3} ml/mc-hr in dry air.

The reaction rate was found to be independent of oxygen concentration and surface area at constant total pressures above 100 mm but to drop off sharply below this value.

The rate in oxygen is increased threefold in the presence of water vapor. The rate in atmospheric air, although poorly reproducible, is essentially the same as in dry air.

UNCLASSIFIED

oxygen and 0.62×10^{-3} ml/mc-hr in dry air.

The reaction rate was found to be independent of oxygen concentration and surface area at constant total pressures above 100 mm but to drop off sharply below this value.

The rate in oxygen is increased threefold in the presence of water vapor. The rate in atmospheric air, although poorly reproducible, is essentially the same as in dry air.

UNCLASSIFIED

Naval Radiological Defense Laboratory
USNRDL-TR-565

THE SELF-RADIATION OXIDATION OF TRITIUM
IN OXYGEN AND AIR by G.J. Casaletto, L.H.
Gevantman, and J.B. Nash 8 May 1962 25 p.
table illus. 11 refs. UNCLASSIFIED

The rate of self-radiation oxidation of tritium has
been studied in atmospheres of oxygen
and air by direct analysis of products as
a function of time.

Second-order dependence on tritium
concentration was observed below
1 mc/ml. Rate constants were deter-
mined to be 1.2×10^{-3} ml/mc-hr in
(over)

1. Tritium - Radioactivity.
2. Tritium oxide.
3. Water - Exchange re-
actions.
4. Water vapor - Chemi-
cal reaction.
5. Air - Radioactivation
analysis.
- I. Casaletto, G.J.
- II. Gevantman, L.H.
- III. Nash, J.B.
- IV. Title.
- V. S-F011 05 11.
UNCLASSIFIED

Naval Radiological Defense Laboratory
USNRDL-TR-565

THE SELF-RADIATION OXIDATION OF TRITIUM
IN OXYGEN AND AIR by G.J. Casaletto, L.H.
Gevantman, and J.B. Nash 8 May 1962 25 p.
table illus. 11 refs. UNCLASSIFIED

The rate of self-radiation oxidation of tritium has
been studied in atmospheres of oxygen
and air by direct analysis of products as
a function of time.

Second-order dependence on tritium
concentration was observed below
1 mc/ml. Rate constants were deter-
mined to be 1.2×10^{-3} ml/mc-hr in
(over)

1. Tritium - Radioactivity.
2. Tritium oxide.
3. Water - Exchange re-
actions.
4. Water vapor - Chemi-
cal reaction.
5. Air - Radioactivation
analysis.
- I. Casaletto, G.J.
- II. Gevantman, L.H.
- III. Nash, J.B.
- IV. Title.
- V. S-F011 05 11.
UNCLASSIFIED

oxygen and 0.62×10^{-3} ml/mc-hr in dry air.

The reaction rate was found to be independent of oxygen concentration and
surface area at constant total pressures above 100 mm but to drop off sharply below
this value.

The rate in oxygen is increased threefold in the presence of water vapor. The
rate in atmospheric air, although poorly reproducible, is essentially the same as
in dry air.

UNCLASSIFIED

oxygen and 0.62×10^{-3} ml/mc-hr in dry air.

The reaction rate was found to be independent of oxygen concentration and
surface area at constant total pressures above 100 mm but to drop off sharply below
this value.

The rate in oxygen is increased threefold in the presence of water vapor. The
rate in atmospheric air, although poorly reproducible, is essentially the same as
in dry air.

UNCLASSIFIED

<p>Naval Radiological Defense Laboratory USNRDL-TR-565</p> <p>THE SELF-RADIATION OXIDATION OF TRITIUM IN OXYGEN AND AIR by G.J. Casaletto, L.H. Gevantman, and J.B. Nash 8 May 1962 25 p. table illus. 11 refs. UNCLASSIFIED</p> <p>The rate of self-radiation oxidation of tritium has been studied in atmospheres of oxygen and air by direct analysis of products as a function of time.</p> <p>Second-order dependence on tritium concentration was observed below 1 mc/ml. Rate constants were determined to be 1.2×10^{-3} ml/mc-hr in (over)</p>	<ol style="list-style-type: none"> 1. Tritium - Radioactivity. 2. Tritium oxide. 3. Water - Exchange reactions. 4. Water vapor - Chemical reaction. 5. Air - Radioactivation analysis. <ol style="list-style-type: none"> I. Casaletto, G.J. II. Gevantman, L.H. III. Nash, J.B. IV. Title. V. S-F011 05 11. <p>UNCLASSIFIED</p>
<p>Naval Radiological Defense Laboratory USNRDL-TR-565</p> <p>THE SELF-RADIATION OXIDATION OF TRITIUM IN OXYGEN AND AIR by G.J. Casaletto, L.H. Gevantman, and J.B. Nash 8 May 1962 25 p. table illus. 11 refs. UNCLASSIFIED</p> <p>The rate of self-radiation oxidation of tritium has been studied in atmospheres of oxygen and air by direct analysis of products as a function of time.</p> <p>Second-order dependence on tritium concentration was observed below 1 mc/ml. Rate constants were determined to be 1.2×10^{-3} ml/mc-hr in (over)</p> <p>oxygen and 0.62×10^{-3} ml/mc-hr in dry air.</p> <p>The reaction rate was found to be independent of oxygen concentration and surface area at constant total pressures above 100 mm but to drop off sharply below this value.</p> <p>The rate in oxygen is increased threefold in the presence of water vapor. The rate in atmospheric air, although poorly reproducible, is essentially the same as in dry air.</p>	<ol style="list-style-type: none"> 1. Tritium - Radioactivity. 2. Tritium oxide. 3. Water - Exchange reactions. 4. Water vapor - Chemical reaction. 5. Air - Radioactivation analysis. <ol style="list-style-type: none"> I. Casaletto, G.J. II. Gevantman, L.H. III. Nash, J.B. IV. Title. V. S-F011 05 11. <p>UNCLASSIFIED</p>

UNCLASSIFIED

UNCLASSIFIED

<p>Naval Radiological Defense Laboratory USNRDL-TR-565</p> <p>THE SELF-RADIATION OXIDATION OF TRITIUM IN OXYGEN AND AIR by G.J. Casaletto, L.H. Gevantman, and J.B. Nash 8 May 1962 25 p. table illus. 11 refs. UNCLASSIFIED</p> <p>The rate of self-radiation oxidation of tritium has been studied in atmospheres of oxygen and air by direct analysis of products as a function of time.</p> <p>Second-order dependence on tritium concentration was observed below 1 mc/ml. Rate constants were determined to be 1.2×10^{-3} ml/mc-hr in (over)</p>	<ol style="list-style-type: none"> 1. Tritium - Radioactivity. 2. Tritium oxide. 3. Water - Exchange reactions. 4. Water vapor - Chemical reaction. 5. Air - Radioactivation analysis. <ol style="list-style-type: none"> I. Casaletto, G.J. II. Gevantman, L.H. III. Nash, J.B. IV. Title. V. S-F011 05 11. <p>UNCLASSIFIED</p>
<p>Naval Radiological Defense Laboratory USNRDL-TR-566</p> <p>THE SELF-RADIATION OXIDATION OF TRITIUM IN OXYGEN AND AIR by G.J. Casaletto, L.H. Gevantman, and J.B. Nash 8 May 1962 25 p. table illus. 11 refs. UNCLASSIFIED</p> <p>The rate of self-radiation oxidation of tritium has been studied in atmospheres of oxygen and air by direct analysis of products as a function of time.</p> <p>Second-order dependence on tritium concentration was observed below 1 mc/ml. Rate constants were determined to be 1.2×10^{-3} ml/mc-hr in (over)</p>	<ol style="list-style-type: none"> 1. Tritium - Radioactivity. 2. Tritium oxide. 3. Water - Exchange reactions. 4. Water vapor - Chemical reaction. 5. Air - Radioactivation analysis. <ol style="list-style-type: none"> I. Casaletto, G.J. II. Gevantman, L.H. III. Nash, J.B. IV. Title. V. S-F011 05 11. <p>UNCLASSIFIED</p>
<p>oxygen and 0.62×10^{-3} ml/mc-hr in dry air.</p> <p>The reaction rate was found to be independent of oxygen concentration and surface area at constant total pressures above 100 mm but to drop off sharply below this value.</p> <p>The rate in oxygen is increased threefold in the presence of water vapor. The rate in atmospheric air, although poorly reproducible, is essentially the same as in dry air.</p>	<p>oxygen and 0.62×10^{-3} ml/mc-hr in dry air.</p> <p>The reaction rate was found to be independent of oxygen concentration and surface area at constant total pressures above 100 mm but to drop off sharply below this value.</p> <p>The rate in oxygen is increased threefold in the presence of water vapor. The rate in atmospheric air, although poorly reproducible, is essentially the same as in dry air.</p>

UNCLASSIFIED

UNCLASSIFIED