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Informal Report

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Methane Generated from Graphite-Tritium Interaction

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Methane Generated from Graphite-Tritium Interaction

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METHANE GENERATED FROM GRAPHITE-TRITIUM INTERACTION

by

D. O. Coffin and C. R. Walthers

ABSTRACT

When hydrogen isotopes are separated by cryogenic distillation, as little as 1 ppm of methane will eventually plug the still as frost accumulates on the column packings. Elemental carbon exposed to tritium generates methane spontaneously, and yet some dry transfer pumps, otherwise compatible with tritium, convey the gas with graphite rotors. This study was to determine the methane production rate for graphite in tritium. A pump manufacturer supplied graphite samples that we exposed to tritium gas at 0.8 atm. After 137 days we measured a methane synthesis rate of 6 ng/h per cm^2 of graphite exposed. At this rate methane might grow to a concentration of 0.01 ppm when pure tritium is transferred once through a typical graphite-rotor transfer pump. Such a low methane level will not cause column blockage, even if the cryogenic still is operated continuously for many years.

I. INTRODUCTION

Since manmade tritium was first produced, researchers have sought a reliable, noncontaminating, tritium-compatible transfer pump that would be useful from one atmosphere down to moderate vacuum (less than 100 Pa). Most mechanical vacuum pumps rely upon some combination of lubricating oils and elastomeric seals to transmit motion, to seal rotary or reciprocating shafts, and/or to lubricate internal moving parts. Because tritium is incompatible with all organic materials, such pumps have severely limited lifetimes when exposed to tritium, and if the pump fails prematurely, it is likely to release an unacceptable quantity of radioactive tritium to the environment.

Several transfer pumps are now available that displace gases with a reciprocating metal bellows* or metal diaphragm,** so internal lubrication and elastomeric seals can be eliminated. Because these designs have inherent dead volumes and rely upon check valves, their vacuum performance is quite limited. Using another approach, one manufacturer*** has developed a promising pump that has a minute dead volume and no check valves. The pump works by squeezing the gas out between a pair of mutually orbiting, self-lubricating graphite rotors. Other manufacturers also offer dry vacuum pumps that use graphite rotors or vanes.†,‡

*Metal Bellows Corporation, 1075 Providence Highway, Sharon, MA 02067

**Pressure Products Industries, 900 Louis Drive, Warminster, PA 18974

***Arthur D. Little, Inc., Acorn Park, Cambridge, MA 02140

†Edwards High Vacuum Inc., 3279 Grand Island Blvd., Grand Island, NY 14072

‡Gast Manufacturing Corp., P.O. Box 117, Benton Harbor, MI 49022

Although graphite can substitute for liquid lubricants in gas transfer pumps, it may not be suitable in tritium systems because of recent evidence that tritium spontaneously synthesizes methane when exposed to small amounts of carbon.[1] This synthesis, normally sluggish at room temperature, is accelerated by the ionization energy from tritium beta decay (Fig. 1). We wanted to measure the rate of methane formation when graphite was exposed to tritium in a typical transfer pump geometry.

II. THE EXPERIMENT

Arthur D. Little, Inc. provided four checker-size disks of graphite for our exposure tests. Two of these, designated as PO-3, were pure cast carbon graphite; the other two, designated as PBH-33, were surface impregnated with zinc phosphate. Before loading the samples into the test cylinders, we measured the mass and dimensions of each disk. We assembled the test cylinders from standard Varian ConFlat flanges, which are sealed with copper compression gaskets and can maintain their integrity under wide conditions of thermal cycling and mechanical stress. A typical test vessel and its enclosed graphite disk are illustrated in Fig. 2. The double valve at one end permitted us to withdraw less than 1 cm^3 (STP) whenever we needed an analytical sample. The cylinders, which averaged 120 cm^3, were thus not significantly depleted by the few samples taken.

Table I lists the samples and the gases to which they were exposed. Morris[1] reported that methane was generated when tritium gas reacted with the interstitial carbon exposed at the surface of type 304 stainless steel, but he saw no corresponding methane formation with deuterium. We included sample 2 (tritium and stainless steel) and sample 3 (deuterium and graphite) to verify and extend these earlier observations.

TABLE I

GRAPHITE SAMPLES AND EXPOSURES

Cylinder No.	Graphite	Gas	kPa at 300 K
1	PO-3, PBH-33	Tritium	79.5
2	None	Tritium	79.6
3	PO-3	Deuterium	79.5

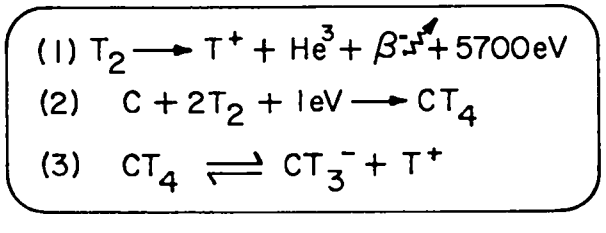

Fig. 1
Spontaneous formation of tritiated methane.

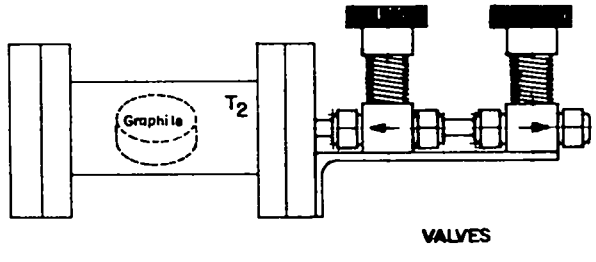

Fig. 2
Graphite-tritium exposure sample.

III. RESULTS

During the exposure, we periodically sampled gas from the three test cylinders on a quadrupole mass spectrometer. Although we detected the characteristic methane peaks in the two tritium containers, deficiencies in our analytical sampling system prevented us from making a quantitative comparison.

After 137 days we analyzed all the gas samples again on a magnetic sector mass spectrometer. We determined the instrument's methane sensitivity by running a standard sample, prepared from pure gases, of 99% D_2 and 1% CH_4.

Table II shows that the most methane was generated by the graphite-tritium sample, as we had anticipated. We also observed a significant growth of methane in the stainless steel cylinder containing only tritium gas, thus confirming Morris's work. The 137-day tritium exposure yielded 16 cm^3 (STP) of methane per m^3 of stainless steel, which had received no special cleaning or surface treatment. This agrees well enough with Morris's observed rate of 8-10 cm^3/m^2 for ultrasonically degreased stainless steel, exposed for 120 days. We detected no methane in the deuterium-graphite sample, confirming that methane synthesizes at a negligible rate at low temperatures, unless ionizing radiation is present.

Table II also reveals that the concentration of normal hydrogen (H_2) increased in both tritium samples during the exposure period. Such hydrogen growth, which always occurs in tritium stored in stainless steel vessels, results from the exchange of gaseous tritium with hydrogen dissolved in the container walls. The additional hydrogen observed in the graphite-tritium sample probably results from isotopic exchange with water originally adsorbed on the graphite, as these samples were not baked before exposure.

Because all hydrocarbons adsorb on charcoal at room temperature, we wanted to ensure that no additional methane had escaped the gas phase by physical adsorption on the graphite. We therefore heated the graphite-tritium sample successively to 200°C and 400°C and ran additional mass spectra at each temperature. No significant change in methane composition was observed, therefore, we conclude that essentially all spontaneously synthesized methane in the graphite-tritium system remains gaseous at ambient temperature.

Finally, after completing the analytical work, we recovered the gas from the test containers and removed the graphite specimens for physical examination. Except for the expected high levels of beta activity of the tritium exposed samples, there were no obvious physical differences between specimens exposed to tritium or deuterium and the control held at ambient laboratory conditions for the same period. Within the precision of our measurements, dimensions, mass, and physical appearance remained invariant for all samples.

TABLE II

GAS ANALYSIS[a] AFTER 137 DAYS

Gas	Tritium (Original)	Tritium PO3, PBH33	Tritium Stainless Steel	Deuterium PO3
T_2	95.6%	86.9%	90.6%	---
D_2	4.2	3.6	3.7	99.6%
H_2	0.2	4.7	1.4	0.4
He-3	---	3.7	3.9	---
Methane[b]	---	1.1	0.4	---

[a]As measured on a Consolidated Electrodynamics Corporation 21-620 Mass Spectrometer

[b]Aggregate of $C(H,D,T)_4$ and $C(H,D,T)_3$

IV. CONCLUSIONS

Using our measured methane synthesis rate, the surface area of the graphite rotors in the proposed Arthur D. Little pump, and its designed volumetric displacement, we calculate that methane would rise to a concentration of approximately 0.01 ppm if tritium were transferred once through at standard atmospheric pressure. This low methane level does not constitute a cryogenic plugging hazard. Of course, if tritium is continuously recirculated through such a pump, methane concentration will continually increase until it is removed by freezing or chemical treatment. If graphite components are not baked out under vacuum before they are exposed to tritium, exchange between T_2 and adsorbed H_2O will cause high levels of hydrogen impurity and a concurrent loss of tritium, which cannot be readily recovered. Therefore, each requirement for a transfer pump must be analyzed to determine whether a graphite containing device is suitable. A graphite-rotor pump could be used to inject a small controlled quantity of methane into the gas stream, as must be done in the Impurity Simulator (IMP).

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REFERENCE

1. G. A. Morris, "Methane Formation in Tritium Gas Exposed to Stainless Steel," Lawrence Livermore Laboratory report UCRL-52262 (March 25, 1977).

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