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TRITIUM RETENTION IN
EBR-II-IRRADIATED BORON CARBIDE

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ABSTRACT

The retention and loss of tritium from EBR-II-irradiated boron carbide were investigated. The tritium content of the irradiated samples, analyzed by chemical dissolution followed by liquid-scintillation counting, showed that essentially all the tritium produced by the nuclear processes is retained by the boron carbide. Rates of tritium evolution after irradiation were measured by heating samples in a carrier-gas stream and collecting the evolved tritium; rates of evolution were obtained as a function of temperature of the B_4C during the heat treatment, the time of heating, and the atmosphere surrounding the sample. The results reveal that tritium is substantially retained in B_4C at temperatures higher than those experienced by EBR-II high-worth control rods. However, considerable loss of tritium occurs at temperatures above $700^\circ C$. A theoretical model, based on the crystal structure of B_4C , the properties of the tritium-producing nuclear reactions, the mechanism of recoil slowing down and trapping, and posttrapping phenomena, is presented; the model qualitatively accounts for the observed retention and loss of tritium.

I. INTRODUCTION

The refractory and neutron-absorbing properties of boron carbide would appear to make it an ideal material to be used in the control rods of high-temperature liquid-metal fast breeder reactors (LMFBR's). Because of these favorable characteristics, high-density B_4C pellets in high-worth control rods have been tested in EBR-II, and their utilization in the Fast Flux Test Facility (FFTF) is planned. However, a potentially serious difficulty with B_4C is the production of tritium from nuclear reactions, tritium that may be lost to the sodium coolant and eventually released to the atmosphere. Estimates made to date of the tritium inventory of the primary sodium coolant of fast reactors have assumed 100% loss of the tritium produced in B_4C to the coolant, analogous to the loss of ternary-fission tritium from the fuel to the coolant. Certainly, if tritium is released from the B_4C matrix at operating temperatures, it will diffuse rapidly through the stainless steel cladding to the sodium coolant.

Tritium is formed in boron carbide by neutron reactions with both isotopes of boron,

The high threshold value for Reaction 2 would preclude the reaction with ^{11}B from contributing significantly to the production of tritium in a reactor. However, calculations show that the amount of tritium produced from ^{10}B may equal or exceed that from ternary fission of the fuel in reactors controlled solely with high-worth control rods (HWCR's) of B_4C , depending on the bank-position of the rods.

Lithium is produced in the B_4C from ^{10}B according to the reaction

which accounts for the major ^{10}B burnup. About 720 atoms of ^7Li are produced for each atom of ^3H ; this, as discussed later, is important to the retention of ^3H in B_4C at temperatures below 700°C .

To determine the extent of tritium retention in the B_4C irradiated in an EBR-II HWCR, samples from the B_4C pellets were dissolved chemically and the released tritium converted to tritiated water, which was measured by liquid-scintillation counting techniques. The measured values were compared to the calculated ^3H production.

Because of the importance of tritium loss from boron carbide control rods, we also investigated the evolution of tritium from heated pieces of B_4C weighing 100-200 mg, which had been part of a 14-in. section of natural boron carbide used as a fuel follower in rod HWCR-L-4009S of EBR-II. The control rod is shown in Fig. 1. Rates of tritium evolution were studied as a function of the temperature of the sample in the heat treatment, the time of heating, and the atmosphere surrounding the pieces. In the heat-treatment experiments, the temperature and the composition of the carrier gas flowing past the samples were carefully controlled, while the evolved tritium was collected in increments as tritiated water for the activity measurements. A theoretical model, based on the crystal structure of the boron carbide, the characteristics of the nuclear reactions, recoil slowing down and trapping, and posttrapping phenomena, has been developed to account qualitatively for the experimental results.

II. EXPERIMENTAL PROCEDURES AND RESULTS

A. Irradiation of High-worth Control Rod

The boron carbide samples used in the present study were removed from a 14-in. section of natural B_4C in a high-worth control rod (HWCR-L-4009S)

Fig. 1. Diagram of High-worth Control Rod, Showing Position of B_4C Pellets. ANL Neg. No. Q5366.

(Fig. 1), which had been removed from EBR-II on March 27, 1972, after 6804 MWD of radiation. The hardware and B_4C have been examined for radiation effects.¹

The in-reactor operating temperatures of the B_4C portion of the HWCR were calculated to be 576°C (1070°F) for the pellet surface and 604°C (1120°F) for the pellet centerline in the region nearest the core center. In the region farthest from the core center, the pellet surface temperature was 547°C (1017°F) and the centerline temperature was 552°C (1027°F).

B. Comparison of Measured and Calculated Tritium Concentrations in Boron Carbide

With the method described in the appendix, several samples of B_4C from capsule O, HWCR-L-4009S, were analyzed for tritium content. Briefly, samples of B_4C weighing 100-200 mg were fused in NaOH at 700°C in a silver crucible. The released tritium was converted to water by oxidation over CuO, collected, and counted by a liquid-scintillation technique. Figure 2 compares the measured values for tritium retained in the B_4C , expressed as the number of tritium atoms per ^{10}B atom, to the calculated tritium production values. The calculated tritium production values are from Sehgal and Rempert, ANL (solid line),² and Lippincott, HEDL (three points indicated by X's).³ The measured values represent multiple analyses of the same pellet, all of which were within $\pm 5\%$ of the average value. The measured tritium retained in the B_4C is seen to be approximately equal to or greater than the calculated production. This indicates that probably very little of the tritium produced in the B_4C is lost at EBR-II operating temperatures (550-600°C). Uncertainties in the neutron fluxes and in the effective cross section for tritium production

Fig. 2. Measured 3H in Irradiated B_4C , Compared with Calculated Production of 3H , as a Function of Position in Control Rod

probably account for the differences between calculated and measured values. Consistent with observations on other nuclear reactions, the disagreement becomes greater as the distance from the reactor core center increases.

C. Heating Experiments

Since the above results establish that virtually all the tritium is retained in the B_4C at EBR-II operating conditions, the important remaining questions are how the tritium is bonded in the B_4C and how firmly it is held. In the first experiments, B_4C was heated at various temperatures in air and in argon containing different concentrations of oxygen. Samples of B_4C weighing 100-200 mg were heated in a flowing stream of gas, which was then passed over CuO to oxidize liberated 3H to 3H_2O . The 3H_2O was passed into cold water, which was sampled at intervals for scintillation counting. The fraction of 3H removed from the sample of B_4C was plotted against heating time in hours. The fraction lost was computed on the basis of the total found in the pellet by chemical analysis.

It became immediately clear that oxygen inhibits the loss of 3H from B_4C by forming a glassy coating of B_2O_3 on the sample surface in the temperature range above $700^\circ C$. The inhibiting effect is illustrated in the plots of Fig. 3. At $900^\circ C$, more than 90% of the 3H is lost from a sample heated 70 hr in pure argon, but when heated in air, less than 25% is lost in the same time. Because of this inhibiting effect, in subsequent experiments argon was first carefully purified by passing it over magnesium perchlorate to remove water and then over zirconium at $900^\circ C$ to remove oxygen. The residual concentrations of H_2O and oxygen were probably less than 1 ppb. The purified argon was passed over the heated sample and through CuO to oxidize the 3H to 3H_2O , which was collected and counted as before. The fraction lost from the B_4C at a steady-state temperature was plotted against time. The results in Fig. 4 show that ~90% of the 3H is lost in 20 or more hours from B_4C at $900^\circ C$, and that most of the 3H is retained below $700^\circ C$.

To check the indication that 10% of the 3H was retained after 80 hr at $900^\circ C$, a third very careful experiment was performed. In this experiment, the sample of B_4C was heated to $900^\circ C$ in purified argon, and the liberated 3H was collected in water contained in a gas-wash vessel with a water-vapor trap attached to the outlet. To avoid loss, the collecting water was deliberately not sampled at intervals as before. After a steady-state heating period of 80 hr at $900^\circ C$, the water in the trap was combined with that in the gas-wash vessel. The tritiated water was then diluted to volume and counted. The heated specimen was then dissolved chemically, and the 3H remaining in it was determined. Based upon the measured 3H concentration originally in the B_4C , a material balance showed that the fraction lost on heating was 1.06; i.e., within limits of error, all the 3H was released. The fraction left in the heated sample was 0.001, or again within the limits of error, substantially all the 3H was released. These results demonstrate conclusively that the reason the plot of Fig. 4 does not show complete loss of 3H at $900^\circ C$ is that some of the tritium was lost in the trapping process, in which no attempt had been made to prevent evaporation losses.

Fig. 3
Effect of Oxygen on ^3H Loss
from B_4C at 900°C

Fig. 4
Effect of Heating on ^3H Loss
from B_4C in Pure Argon

III. DISCUSSION

A. Production and Retention of ^3H in B_4C

The experimental studies of tritium retention by high-density boron carbide described in this report indicate that tritium is lost from pile-irradiated material above a temperature of $\sim 650^\circ\text{C}$. Since tritium is released from heated B_4C , it is of importance to understand the mechanism of its production, retention, and loss from the boron carbide lattice. This involved consideration of four determining aspects of the problem:

- (1) The crystal structure of boron carbide and the nature of the chemical bonding in this compound.
- (2) The characteristics of the nuclear reaction that produces tritium (e.g., the energy and state of the tritium recoil) and of other nuclear reactions whose products or effects influence the behavior of the tritium.
- (3) The slowing down of tritium recoils and the properties of the available trapping sites.
- (4) Posttrapping phenomena: diffusion, effects of crystallite impurities and defects, the effects of oxygen and H_2O in the atmosphere surrounding the B_4C , and possible phase changes.

1. Structure and Bonding

Boron carbide possesses a rhombohedral structure (as shown in Fig. 5), whose structural units contain 12 boron atoms, arranged at the vertices of a regular icosahedron, and a linear chain of three carbons.⁴ Thus its chemical formula is actually B_{12}C_3 , rather than the simplified B_4C usually written. Each boron atom has five equidistant boron atoms as nearest neighbors in its own icosahedron, and may also be bonded to an end carbon atom of the linear chain or to a boron atom of an adjacent icosahedral group. The end carbon atoms are each bound to boron atoms of three adjacent icosahedrons, while the middle carbon atom is attached only to the two end carbons.

Fig. 5. Rhombohedral Structure of Boron Carbide.
ANL Neg. No. 103-R5815.

The bond lengths are B-B, 1.74-1.80 Å; B-C, 1.64 Å; C-C, 1.39-1.45 Å. The boron carbide lattice therefore has the appearance of "geodesic domes" tied together at their vertices or through linear chains of three carbon atoms. The bonds between the boron atoms are obviously not electron-pair (covalent), since each atom has only three valency electrons but forms six bonds. Consequently, the bonding is more closely metallic. The attachment of three electron-deficient boron atoms to each

end carbon atom makes it likely that the middle carbon atom is either divalent or connected by double bonds to the other carbons. The three-dimensional structures of boron atoms form very stable lattices, through which valence electrons and, at high enough temperatures, metallic impurity atoms migrate with ease.

2. Nuclear Processes in B₄C

Nuclear processes involved in the neutron irradiation of B₄C were mentioned in Sec. I above. The two reactions of interest to us in this discussion are Reactions 3 and 1:

After exposure of B₄C to the neutron flux of EBR-II, the ratios of products resulting from reactions are approximately $^7\text{Li}:^4\text{He}:^3\text{H} = 720:720:1$. For the B₄C studied here, the ^{10}B "burnup" was 1.5 at. %, which corresponds to 0.24 at. % ^7Li . A determination of lithium in a sample of B₄C gave ~1700 ppm by weight. The calculated value was 1620 ppm, within 5% of that found. Data collected by Patriarca indicate that the lithium occupies interstitial sites randomly distributed within the B₄C lattice, with no evidence of a lithium-rich phase.⁵

Taking into account the isotopic abundance of ^{10}B , we calculate that one boron atom in about 339, or one icosahedron in 28, has been affected during the neutron irradiation. In addition, the structure of B₄C will have been damaged by fast neutrons, high-energy gamma rays, and X rays, and by energy conversion during the slowing down of the energetic recoils from Reactions 1 and 3.

The kinetic exoergicity, Q, of the tritium-producing Reaction 1 is 232 keV, so that the recoil energy of the ^3H is 169 keV.

3. The Mechanism of Slowing Down of Tritium Recoils

Having experienced a recoil of 169 keV, the triton will lose its kinetic energy by several collisions with boron (mainly) and carbon atoms. The principal mode of energy loss at lower kinetic energies is usually nuclear stopping; i.e., by kinetic-energy transfer in collisions of atoms, but at higher energies, electronic stopping contributes greatly.⁶ The latter mechanism may indeed be dominant for tritium ions because of the complete lack of shell electrons in this ion.⁷⁻⁹ In an electron-deficient crystalline lattice such as B₄C, furthermore, the tritium recoil may very well exist as a positive ion over its entire slowing-down path. However, the path length and projected range, i.e., the projection of the actual path length along the initial direction of the recoil, may each be estimated⁹ to be about 10^{-4} cm; consequently, the tritium recoil comes to rest at a relatively great distance from the place of its birth. The time of slowing down is extremely short--less than 10^{-12} sec.

Of far greater importance in determining ^3H retention in boron carbide than the mechanisms of energy loss are the trapping and bonding sites available to the energy-degraded recoil ion. The undisturbed B_4C lattice offers two sites: (a) interstitial space within each icosahedron, and (b) chemical bonding to the middle atom of the linear three-carbon-atom chain. Because of the electron-deficient nature of the B_{12} structural unit, the recoil will probably come to rest, in most cases, as a $^3\text{H}^+$ ion within it, but the high mobility of electrons in the metallic bonds of the B_{12} lattice should favor partial neutralization of the tritons. However, the surplus of electronic charge near the middle of the carbon chain would be expected to promote formation of a strong covalent $\text{C}-^3\text{H}$ bond at that position. In addition to these two "normal" sites, the tritium may be trapped by the far more numerous recoil lithium atoms. The latter have also come to rest within the "geodesic" domes, but should be present as Li^+ ions there; consequently, the tritium trapping by lithium may not occur within the domes, but at grain boundaries to which the ions may migrate rapidly at the ambient temperature of the reactor, and where they may be neutralized by surface electrons. X-ray diffraction, scanning-electron microscopy, and nuclear-magnetic-resonance studies⁵ on irradiated B_4C indicate, however, that the lithium occupies interstitial sites randomly in the lattice. There was no evidence for a second, lithium-rich phase. From these results, it was concluded that the lithium is present as ions in various sites with different quadrupole coupling constants and asymmetry parameters, even when the neutron irradiation occurred at 730°C .⁵ Nevertheless, the absence of a lithium-rich phase does not preclude the presence of numerous lithium atoms dispersed along grain boundaries. Other trapping sites will be at imperfections and lattice vacancies caused by fast-neutron interactions and the nuclear reactions themselves.

4. Posttrapping Effects in B_4C during Irradiation

Diffusion of the thermalized recoil species during the period of irradiation in EBR-II, and trapping by lithium atoms and possibly by carbon atoms in the boron carbide, exert the dominant influences on the extent of retention of tritium in reactor-irradiated B_4C .

Although diffusion rates have not been determined for $^3\text{H}^+$ and Li^+ in B_4C , measurements^{10,11} on metal borides, metal carbohydrides, and silicon semiconductors suggest that, at sufficiently high temperatures, the tritium (as $^3\text{H}^+$) and lithium (as Li^+) as well as the He^+ produced in the nuclear reactions 1-3 diffuse rapidly through the lattice. The diffusion rates of these ionic species may be as high as $10^{-6} \text{ cm}^2 \text{ sec}^{-1}$ or even higher at the reactor temperature; consequently, mean diffusion distances should be of the order of 1 cm after 100 hr of irradiation. ($\bar{S} = \sqrt{dt}$, where $\bar{S}$ = mean diffusion distance, d = diffusion rate, and t = time of heating.) This distance is greater than the radius of an irradiated B_4C pellet. Thus, the calculation indicates a substantial loss of tritium from irradiated B_4C . Since no tritium is released from the pellets during reactor irradiation, the tritium must be chemically trapped. Thermal annealing such as occurs during the reactor irradiation must cause the Li^+ and $^3\text{H}^+$ ions to collect at grain boundaries and surfaces, where they are neutralized by surface electrons and then combine

to form lithium tritide. An alternative destination of the energy-degraded tritium ions could be the central atom of the carbon chain. It is of interest that X-ray analysis⁵ shows that the rhombohedral angle, the unit-cell length, and the volume of reactor-irradiated B_4C all change drastically between 700 and 1000°C, reverting above the higher temperature to their respective values characteristic of unirradiated material. Nevertheless, differential thermal analyses gave no evidence for a phase change in this temperature region.¹² These observations are consistent with the diffusion of the three products of the nuclear reactions out of the lattice to grain boundaries and surfaces.

B. Interpretation of 3H Release Experiments

The fraction of tritium released from compacted boron carbide that had been irradiated in EBR-II is seen from the experimental results to rise rapidly with time, and then either become constant or rise slowly. Both the initial rate of increase and the ultimate fraction of tritium lost are strongly dependent on the temperature of the B_4C , its state of aggregation, and the presence of oxygen in the atmosphere surrounding the heated sample. Below 650°C, no tritium is released, as shown by comparison of the tritium content of a sample with that expected from calculations based on neutron flux, the known reaction cross sections, the number of ^{10}B nuclei, and the length of time of irradiation in EBR-II. If the B_4C is heated to 900°C, and no special purification of the argon entrainment gas is undertaken to remove traces of oxygen (~50 ppm) and H_2O (~200 ppm), about 60% of the tritium is released after 70 hr (see Fig. 3). When special effort is made to remove oxygen and H_2O from the carrier argon, and precautions are taken to minimize evaporation losses, the fraction removed from pieces of the pellet at 900°C is increased ~100%. The presence of very small concentrations of added oxygen (~0.17%) in the atmosphere surrounding the heated sample strongly reduces the amount of tritium released at 900°C. Heating the B_4C in air also causes a marked reduction in loss at 900°C, and is accompanied by massive oxidation of the sample to form a heavy glassy coating of B_2O_3 .

The experimental results therefore are consistent with a mechanism in which the tritium recoils are thermalized and come to rest as ions within the icosahedral arrays. At the temperature of the pellets in the reactor, the ions diffuse rapidly through the lattice to grain boundaries and surfaces, where they are neutralized and trapped by the much more numerous lithium atoms from the $^{10}B(n,\alpha)^7Li$ nuclear reaction, which have also diffused rapidly to grain boundaries and surfaces and have then become neutralized by surface electrons. The formation of stable Li^3H and C^3H bonds (the bond energies are 2.4 and 3.5 eV, respectively) at the ambient temperature of the reactor is responsible for the complete retention of tritium in boron carbide control rods.

The loss of tritium above 650°C in the thermal gas-release experiments reported here is probably a direct result of the decomposition of Li^3H . This may be concluded from the properties of its isotopic analog, LiH . Lithium hydride first begins to decompose in vacuum at 450°C, and the dissociation

pressure (as H_2) increases rapidly in the 800-950°C range.¹³ Our results suggest, furthermore, that the fraction of tritium atoms that may be trapped by chemical combination with the middle carbon atoms of the three-member side chains appear to be very slight, despite the stronger bond expected, since from the 3H release experiments, they appear to comprise almost none of the recoils.

APPENDIX

Analytical Method

1. Introduction

A simple and rapid method was required to determine the amount of ^3H in B_4C . A chemical reaction that would completely consume the B_4C was considered as the best approach, since this would give the proper conditions to release all the ^3H either as the element, as water, or as some other volatile compound.

Attempts to burn the B_4C in pure oxygen were unsuccessful, because a glaze of B_2O_3 formed on the surface and slowed further reaction to an imperceptible rate. Fusion of B_4C with Na_2O_2 gave an explosively reactive mixture. Also, the melt was very difficult to contain because of the high heat of reaction and the extremely corrosive properties of the Na_2O_2 . The best results were obtained by the fusion technique, with NaOH as the flux. The reaction rate is easily controlled by temperature and proceeds smoothly, and the melt can be contained in a silver crucible.

2. Analytical Method

a. Principle

B_4C is reacted with 20 times its weight of NaOH in a deep-form silver crucible held at $650\text{--}700^\circ\text{C}$. A gas mixture of $\text{He-10\% H}_2$ is passed over the melt to sweep out the ^3H , H^3HO , and any other possible volatiles containing ^3H . This gas mixture is passed over a bed of CuO held at $500\text{--}600^\circ\text{C}$, where tritium or any compound of tritium is converted to tritiated water. The combustion products then pass through a water-cooled condenser, where the tritiated water condenses to a liquid and then passes into a beaker containing water cooled to 0°C .

After the fusion is completed, the crucible is cooled to less than 100°C . Dilute acetic acid is added to the crucible in excess to neutralize completely the unreacted NaOH . The water and any excess acetic acid are then distilled through the CuO bed, the sweep gas mixture being a mechanical aid for carrying the vapor. This procedure removes the last traces of ^3H held in the melt and transfers it as tritiated water to the cooled beaker.

The tritiated water in the beaker is then diluted to 100 ml, and the amount of ^3H determined by liquid-scintillation counting.

b. Apparatus

The apparatus used in the chemical determination of total tritium in B_4C is shown in Fig. 6.

Fig. 6. Diagram of Apparatus for Determination of Total Tritium Content of Boron Carbide. ANL Neg. No. 103-R5818.

The hydrogen and helium inlet lines A and B are 1/8-in. copper tubes, which conduct the gases from standard pressure regulators fed by pressurized-gas bottles. The flow-regulating needle valves C and flow-indicating meters D may be any type capable of regulating and reading helium flow from 6 to 100 ml/min and hydrogen flow from 5 to 50 ml/min. The sweep-gas inlet line E may be rubber or copper, but should be easily manipulated, since it is attached and removed several times during the analysis.

The neutralizing-acid container K is a modified 60-ml Pyrex separatory funnel with a Teflon stopcock. The brass connecting adapter J is made of silver-soldered, spherical-ground brass fittings and a short piece of 1/8-in. soft-copper tubing.

The Pyrex connecting adapter I is made of a female 34/45 standard-taper joint, and is wrapped with a heating tape (152 W), so that its entire outer surface can be heated above 100°C. The heating tape is attached with a woven-glass sticky tape. The adapter is insulated to prevent heat loss by a layer of the sticky tape on the outside of the heating tape. The heating tube G is made of a quartz male 34/45 standard-taper joint and a piece of standard-wall quartz tubing of matching diameter. The heating tube is heated by an electric multiunit tube furnace F, which was rewired to give 1200 W for rapid response in heating. The furnace is 10 in. long and will take a 1 1/4-in. tube. The power to the furnace is delivered by a controller that senses the temperature through a 1/16-in. stainless-sheathed Chromel-Alumel thermocouple. The thermocouple is placed about midway in the side of the furnace to sense the temperature at about the point where the bottom of the silver fusion crucible is located. When desired, this high-wattage furnace is cooled with an air blast directed from the bottom.

The copper oxide bed L is made of tightly packed fine copper turnings inside a quartz tube, which is ~10 in. long and 30-35 mm in outside diameter. The copper oxide is prepared by heating the copper to $600 \pm 10^\circ\text{C}$ and passing air through it at ~200 ml/min for 18-24 hr. The heater for the copper oxide bed is a 10-in.-long, 584-W multiunit tube furnace, capable of taking a tube with 30 to 35-mm OD. The controller for this furnace senses the temperature by a Chromel-Alumel thermocouple placed outside the tube at the midpoint of the CuO bed.

The condenser M is an ordinary, straight-tube type of 10 to 15-mm ID, with a narrow cooling jacket. The lower end of the condenser is fitted with a frit O, which breaks up the gas stream into fine bubbles as it passes into water contained in the 100-ml condensate-collecting beaker P. The beaker is cooled in an ice bath in a shallow 1-liter crystallizing dish N.

For the determination of tritium content of the condensate, a liquid-scintillation counter was used. The counter had an efficiency for ^3H alone of about 30%.

c. Procedure

Weigh a clean dry piece of B_4C (0.1-0.2 g), and transfer to the silver fusion-crucible. Add 20 times this weight of NaOH (reagent grade), in pellet form, to the fusion crucible. Lubricate the ground surfaces of all the inner members of each joint with Dow-Corning Vacuum Grease. Slip the silver crucible into the quartz heating tube, and assemble the apparatus as shown in Fig. 6, but without the neutralizing-acid container, attaching the gas-inlet line E directly to the brass connecting adapter J.

Heat the copper oxide bed to $600 \pm 10^\circ C$. Establish a flow rate of 90-100 ml/min for the helium and 5-15 ml/min for the hydrogen. Place about 20 ml of distilled or demineralized water in the 100-ml condensate beaker. Check to be certain that bubbles through the frit are indicating flow, as this will serve as a rough leak check. After making certain that the apparatus is leak-tight, adjust the temperature of the tube-furnace heater to $600-700^\circ C$. Heat the silver crucible for 90 min at $600-700^\circ C$; then remove the gas-inlet line. Remove the quartz heating tube with the Pyrex-glass adapter attached, and allow the assembly to cool to $<100^\circ C$. In the meantime, cool the furnace to $<100^\circ C$ with an airblast directed up through the heating zone. When the furnace and fusion assembly are cooled, reassemble the equipment as shown in Fig. 6, with the neutralizing-acid container in place. Pour 25 ml of 25% acetic acid into the acid container, and open the stopcock. Place the plug in the acid container and seat it tightly, so as to force the acetic acid into the silver fusion-crucible. Allow the gas to bubble through the solution in the silver fusion crucible for ~10 min; then raise the temperature of the furnace to $\sim 120^\circ C$, and allow this heating rate to continue for 1 hr. After 1 hr, raise the furnace temperature to $200^\circ C$ for 30 min, then to $400^\circ C$ for 30 min. At the end of this neutralization-distillation procedure, turn off the hydrogen flow and use a heat gun to heat the inlet to the copper oxide bed to force any condensed liquid through the train. Heat the outlet also until all condensed water is well inside the condenser inlet. At this time, the volume of liquid in the condensate beaker should be about 50 ml. Detach the condenser from the outlet of the copper oxide bed. Rinse the inside of the condenser into the condensate beaker with several portions of water. Also rinse the outside of the frit and the lower end of the condenser into the condensate beaker.

Quantitatively transfer the condensate to a 100-ml volumetric flask. Dilute to volume, and prepare the solution for counting.

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