SEARCH FOR ^{3}He and ^{4}He IN ARATA-STYLE PALLADIUM CATHODES II: EVIDENCE FOR TRITIUM PRODUCTION

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ABSTRACT

We have made measurements of ^{3}He, ^{4}He and ^{3}H in a sample containing 2.7% of the gas from the interior of an Arata-style hollow palladium electrode charged with ~ 5 g Pd-black which had undergone electrolysis in D_2O as a cathode for 90 days and then as an anode for a further 83 days. There is no evidence for the much larger amounts of ^{4}He observed by Arata and Zhang in similar experiments. However, we have found a very large concentration of $2.3\pm0.5\times10^{12}$ atoms/cc STP ^{3}He which we believe can be attributed to decay of tritium produced during electrolysis. We cannot specify any direct production of ^{3}He, a result which is also different from the conclusions of Arata and Zhang. The ^{3}He and tritium measurements and the results of a gas analysis using a Finnigan-type mass spectrometer show that at the end of the anodic electrolysis, the electrode void contained $5.8\pm0.7\times10^{13}$ atoms tritium in the gas phase as HT, DT and T_2, and $1.7\pm0.3\times10^{15}$ atoms tritium in the aqueous phase as HTO, DTO and T_2O. At this stage, the gas phase pressure was ~18.8 atm. in a free volume of 0.6 cc, and the total mass of water was ~ 5.7 mg. The gas phase tritium value is viewed as a lower limit for gaseous tritium produced inside the electrode because some of that tritium must have been removed into the D_2O electrolyte during the anodic episode.

^{3}He and ^{4}He measurements were also made in the two samples of the Pd-black and in sections cut from the walls both Pd electrodes. The H_2O electrolyzed samples did not show any evidence of unusually high ^{3}He and/or ^{4}He, but all the D_2O electrolyzed samples showed clear evidence of ^{3}He from tritium decay. A stepwise temperature heating experiment performed with a 24.9 mg sample of the D_2O Pd-black showed that the diffusion process for ^{3}He can be described by an equation of the form $D = D_0\exp(-U/kT)$ with an activation energy U of 1.1 eV. It is also apparent that the ^{3}He from tritium is quantitatively retained in the Pd-black at room temperature.

INTRODUCTION

Observation of excess heat in D_2O electrolysis with Pd cathodes was first claimed in 1989 by Fleischmann and Pons who attributed the effect to fusion of deuterium nuclei ([1]). Subsequently, many attempts have been made to confirm this observation and to search for other signatures of D-D fusion under similar conditions. These attempts have met with varying degrees of success and failure. The reader is referred to detailed reviews presented by Storms ([2]) and Nagel ([3]), and to several books ([4], [5], [6]).

In 1990, Arata and Zhang repeated the Fleischmann-Pons experiment and claimed that they had detected neutrons, "sometimes reaching 10^8 n/s, or more" from heavy water cells ([7], [8], [9]). In 1995, Arata and Zhang reported that after D_2O electrolysis, they had detected large amounts of ^4He, approx 10^{16} - 10^{17} atoms/mg, in Pd-black powder sealed under vacuum in specially prepared hollow Pd cathodes ([10]). These results were obtained by heating the Pd-black to 1500 K in a vacuum system attached to a statically-operated quadrupole-type mass spectrometer. The results were stated to be "fully repeatable" ([10]). In 1996, these authors reported that they had confirmed the aforementioned ^4He observation, that they had also detected ^3He with $^3He/^4He \sim 0.25$, and that ^3He or ^4He were not detected in comparable electrolysis experiments using H_2O instead of D_2O ([11]). In subsequent papers, Arata and Zhang ([12], [13], [14], [15]) reported additional data obtained with their mass spectrometric technique, and restated their claims regarding production of excess ^3He and ^4He in Pd-black from the interior of Pd cathodes during D_2O electrolysis.

Although we have experienced some difficulties in understanding the details of the ^3He and ^4He observations of Arata and Zhang, that does not diminish their profound significance if the observations are confirmed. In this connection, Clarke ([16]) has described a recent search for ^3He and

[4]He in four Pd-black samples which had been provided by Professors Arata and Zhang. This search revealed no evidence for the very high [3]He and [4]He concentrations found by Arata and Zhang in similar specimens of Pd-black. However, it should also be mentioned that in a recent paper (18), three of the present authors have reported observations of significant excess heat generated during D_2O electrolysis using an Arata-style hollow palladium cathode.

This paper describes helium isotope investigations of gas samples and Pd-black samples from the interior of Arata-style Pd cathodes which had undergone electrolysis in H_2O and D_2O at Stanford Research International (SRI). The initial helium isotope measurements were made at Pacific Northwest National Laboratory (PNNL) and the samples were then sent to McMaster University (McM) for further analysis using a mass spectrometer which was more sensitive for [3]He.

EXPERIMENTAL METHODS

Electrolysis

For the sake of clarity, it is desirable to give a brief description of the Arata-style cathode and the electrolysis as carried out at SRI. The cathode consists of a Pd cylinder of length = 6.0 cm., O.D. = 1.4 cm., and I.D.= 0.7 cm. The inner volume of 1.1 cc was charged with 5g Pd-black, leaving a free inner volume of ~ 0.6 cc. The cathode was pumped out in a vacuum system and the top piece and body were sealed by electron-beam welding. Two such sealed cathodes were provided by Professor Y. Arata. One was placed in D_2O and the other in H_2O. Sustained electrolysis commenced on October 31, 1998, and ended on January 29, 1999. The electrodes remained in open circuit until

February 27, 1999 when the electrode polarity was reversed, and electrolysis continued until May 11, 1999. A detailed description of all the pertinent features of the electrodes and the electrolysis is given by McKubre et al. ([18]).

Gas Sampling

After electrolysis was completed, both palladium electrodes were sent to PNNL where they were placed in a specially constructed vacuum device attached to the sample line of a Finnigan-type analytical mass spectrometer. The essential features of this device are shown in Figure 1. After an overnight pump, a sharp probe attached to a vacuum bellows was used to puncture the top of the electrode, releasing the trapped gas to the vacuum system. The H_2O electrode was observed to be broken following removal from the electrolysis system at SRI. At the time, it was assumed that high internal pressure had ruptured the circumferential weld near the electrode top. Later examination of the electrode, however, showed that the top of the electrode had not been welded to the body. However, the H_2O electrode was punctured as a test of the extraction system and the puncturing device. Following this test, the D_2O electrode was punctured on September 1, 1999. Because of a failure of a pressure sensor in the expansion volume, 90.6% of the electrode gas was pumped away after a 5 min. equilibration time. After a second expansion and subsequent mass spectrometer analysis, 29% of the remaining sample which represented 2.7% of the electrode gas was stored in a 41.6 cc stainless steel cylinder with a high vacuum valve at one end. Pressure and temperature readings of 21.9 Torr and 26.5 ^{0}C indicated that the steel cylinder contained 1.09 cc STP gas. We estimate that the uncertainty of this number is ± 2%.

Gas Analysis

Three mass spectrometers were employed in the present study. The Finnigan instrument at PNNL is used for rapid analysis of major components of gas samples. The helium mass spectrometer at PNNL is a statically operated machine used for isotopic analysis of small helium samples at a mass resolution of 1 part in 100 ([19], [20]). The helium mass spectrometer at McM is also statically operated, and has a mass resolution of 1 part in 620, which is sufficient to clearly separate ^{3}He from the isobaric species HD and H_3 ([16], [21], [22]). The detection limits for ^{4}He in the PNNL and McM instruments are comparable, approximately 10^8 atoms, but the ^{3}He detection limit of the McM instrument, about 10^4 atoms, is several orders of magnitude lower than that for the PNNL instrument because of the difference in mass resolution and other factors. The detailed sequence of analyses using these three mass spectrometers will be described in the following sections.

RESULTS AND DISCUSSION

Finnigan Data

The Finnigan gas analysis results are given in Table I. The percentage as H_2O, HOD and D_2O is 74.5% which at first glance is surprisingly large. As mentioned previously, pressure and temperature were 21.9 Torr and 26.5 ^{0}C in the Finnigan vacuum system at the time the sample cylinder was isolated. Using this information and the known volumes of the puncturing device and those in the Finnigan vacuum system, and assuming no serious H-D fractionation during gas expansion, we calculate that before the electrode was punctured, its free volume of ~ 0.6 cc

contained approximately 5.7 mg liquid water, 0.015 mg water vapor, and gas (H_2 + HD + D_2 + N_2 + O_2 + N_2O) in the proportions given in Table I at a pressure of about 18.8 atmospheres.

It is apparent that the gas sample analyzed by the Finnigan mass spectrometer was not in isotopic equilibrium for H and D. If we insert the measured values for H_2, HD and D_2 into the isotopic formulae given by Fischer et al. [23] and by Kirshenbaum [24], the predicted equilibrium concentration for D in the water is 60 mole percent. The measured value is 43 mole percent which indicates that D is depleted in the water or that D is enhanced in the gas relative to H. It does not seem possible to attribute this effect to partial pressure differences between H_2O, HOD and D_2O during the expansion steps in the Finnigan vacuum system. Although the sequence and timing of sample handling may have caused minor enhancement of D in the water this is in the opposite direction to the observed effect. We believe that the observed disequilibrium is mainly due to H-D isotopic fractionation which occurred during partial removal of H_2, HD and D_2 from the electrode interior during the anodic electrolysis due to the higher rate of H absorption at the inner wall. At the end of this process, D/H in the gas phase inside the electrode must have been considerably higher than the value before the anodic phase began. It is possible that the apparent H-D water-gas disequilibrium is due to incomplete establishment of H-D isotopic equilibrium during the time between the end of the anodic electrolysis on May 11, 1999 and puncturing the electrode on September 1, 1999.

Initial Helium Measurements in the Electrode Gas Sample

The 41.6 cc stainless steel cylinder containing 1.09 cc STP sample gas was attached to the

inlet line of the PNNL helium mass spectrometer. A 2.4 cc aliquot volume was formed between the cylinder valve and an adjoining metal valve in the inlet system. This volume was accurately measured by determining the ^{4}He content in air trapped at known pressure and temperature between the two valves using a standard isotope dilution procedure with the addition of a known quantity of ^{3}He "spike". A small fraction of the gas mixture was chemically cleaned of active gases with Zr-Al getters (at room temperature) and liquid N_2 - cooled charcoal, and then the fraction was admitted to the mass spectrometer for determination of the ^{3}He/^{4}He ratio. From measurements of the isotopic ratio, the amount of ^{3}He spike, and the known ^{4}He concentration in the atmosphere, the aliquot volume was determined. After the aliquot volume measurement, the system was thoroughly pumped out and two aliquots of sample gas were admitted separately to the mass spectrometer using the same procedure described above except that the sample ^{3}He and ^{4}He ion currents were first measured in a small fraction (~1.4%) of each aliquot. Then a ^{3}He spike was added to the remaining fraction(~98.6%) of each aliquot and a small fraction (~1.4%) of this mixture was analyzed. This procedure allowed an absolute "peak height" calibration of the mass spectrometer. ^{4}He was below the detection limit detection for both aliquots, which is equivalent to an upper limit of ~7×10^{11} atoms/cc STP ^{4}He in the sample cylinder. For one aliquot, the ^{3}He signal in the unspiked sample was below the detection limit, i.e. $\leq 7 \times 10^{11}$ atoms/cc STP ^{3}He in the sample cylinder. The other aliquot showed evidence of a barely detectable amount of ^{3}He which was equivalent to ~1.1×10^{12} atoms/cc STP ^{3}He in the cylinder. When these measurements were complete, the cylinder containing 0.98 cc STP gas was sent to McM for further analysis using the more sensitive ^{3}He mass spectrometer.

Initial Helium Isotope Measurements in the Pd-black Samples

Samples weighing 13 - 17 mg were vaporized in resistance-heated graphite crucibles on line to the PNNL helium mass spectrometer. Details of the procedures including isotope dilution with ^{3}He are given by Farrar and Oliver [20]. The results of the helium isotope measurements on duplicate samples are given in Table II. It appears that in this sense there is no difference between the Pd-black samples used during H_2O and D_2O electrolysis. It is also apparent that there is no evidence for the large amounts of ^{3}He and ^{4}He claimed by Arata and Zhang in Pd-black from similar D_2O electrolysis experiments [10, 11, 12, 13, 14, 15]. When these measurements were completed, the Pd-black samples were sent to McM for further helium isotope analysis.

Helium Isotope and Tritium Measurements in the Electrode Gas Sample.

Soon after arrival from PNNL, the sample cylinder was attached to the McM helium isotope mass spectrometer inlet system. After pump down, the instrument performance was checked carefully by analysis of several standard air aliquots and inlet system blanks as described previously [16, 17]. The sample cylinder valve was cracked open and a small fraction of the gas admitted at 22 ^{0}C to a 34.7 cc volume at a pressure of 1.5 ± 0.3 Torr as determined by a small mercury manometer in the inlet line. The amount of sample admitted to the inlet line was 0.063 ± 0.013 ccSTP. This sample was treated in the usual way by exposure to two activated charcoal traps at liquid N_2 temperature, and to Ti sponge at room temperature [22]. Because of the results obtained in the PNNL analyses described above and in the previous study of Pd-black from Arata-style cathodes [16], it was expected that the sample would contain only very small amounts of ^{3}He and ^{4}He. When the sample was admitted to the mass spectrometer volume, it was shocking to observe a very large signal

of ^{3}He due to 1.4×10^{11} atoms in the static volume. Simultaneous measurement of the ^{4}He ion current gave a value of 1.6×10^{10} atoms for ^{4}He. It should be noted that the ^{3}He sample admitted to the mass spectrometer is large only by comparison with the "usual" ^{3}He samples of 10^5-10^8 atoms, and the instrument detection limit of about 10^4 atoms. The McM measurements gave the following values for the gas in the stainless steel container: ^{3}He = $2.3\pm0.5\times10^{12}$ atoms/cc STP, ^{4}He = $2.5\pm0.7\times10^{11}$ atoms/cc STP. The uncertainties are mainly due to the large error in measurement of pressure.

"Memory effects" for the inert gases are well known to mass spectroscopists, and helium is a special case. In sample handling systems, helium memory is often due to diffusion of remnants of previous samples from glass sections or Viton O-rings. This effect is usually easy to remove by heating the inlet line or by waiting a few days for the effect to disappear. Another type of memory effect is due to ions imbedded from previous samples in interior sections of the instrument. Release of imbedded atoms can cause significant drifts in ion currents when a sample is admitted to the static volume. The bias can be difficult or impossible to correct for when a "dirty" inert gas sample is admitted, i.e. one that contains large amounts of H_2, D_2 or other gases not removed during chemical clean up of the sample. For such samples, until the getter(s) in the mass spectrometer volume has removed the non-inert gases, instrumental mass resolution is seriously degraded, and the experimenter may be unaware of enhanced release of imbedded helium from previous samples. In most cases, the problem is minimized or eliminated by the use of efficient getters in the inlet system and/or in a separate vacuum system and by extrapolating helium ion currents to the time of sample admission to the static volume. In some cases of serious memory, a large sample of N_2 is admitted to the mass spectrometer and the instrument is "scrubbed" by magnetically sweeping the N_2 ion beam back and forth across the tube while using higher than normal ion accelerating voltage.

After the helium isotope analysis of an aliquot of the electrode gas was completed, ^{3}He memory in the mass spectrometer volume was cleaned as described above, but the ^{3}He memory in the sample inlet system could not be completely removed even after several episodes of heating. After a time, it was realized that the memory effect was mainly due to tritium present as HT, DT and TT and/or HTO, DTO, and TTO in the sample. The charcoal traps at liquid N_2 temperature and the Ti sponge trap effectively prevent any tritium from entering the mass spectrometer volume, but a small fraction of tritium must have diffused into the metal sections of the inlet system. Tests showed that the ^{3}He memory was almost entirely due to release of the tritium decay product ^{3}He from certain metal sections in the inlet line. After these sections were replaced, it was decided to make measurements of tritium in the gas and water components of the D_2O electrode gas sample.

These measurements were carried out by a method (22, 25) wherein samples are sealed in low helium permeability (Corning 1720 aluminosilicate glass) containers for suitable decay times prior to assay of accumulated ^{3}He. For this purpose, the cylinder containing the electrode gas sample was attached to a separate vacuum system which had not been previously used for samples high in ^{3}He or tritium. Aliquots of the sample were processed in the following way: After sealing the cylinder to the vacuum system and evacuating, an aliquot of the sample at known temperature and pressure was admitted. The aqueous fraction (H_2O+HOD+D_2O) was condensed in a U-trap at liquid N_2 temperature and the gas fraction (mostly H_2+HD+D_2) pumped quantitatively with a mercury toepler pump into a 1720 glass sample tube which was flame sealed. The liquid N_2 was removed from the U trap and about 30 mg of degassed laboratory distilled water was admitted to the line via a side arm. This water acted as a carrier to allow quantitative recovery of the water in the sample by freezing at liquid N_2 temperature in a 1720 glass sample tube which was flame sealed. The water

carrier introduced a negligible additional amount of tritium because of its low mass and low tritium content ($T/H \sim 30 \times 10^{-18}$). Several aliquots were treated in this way. For some of these, the gas and liquid samples were easily resealed into new 1720 glass sample tubes after the first measurements of accumulated ^{3}He. Decay times varied from 3 to 6 days. Measurements of the tritium concentrations in aliquots of the electrode gas sample received from PNNL gave the following values:

In the H_2, HD and D_2, Tritium= $1.56 \pm 0.20 \times 10^{12}$ atoms/cc STP (N=2)

In the $H_2O+HOD+D_2O$, Tritium= $2.04 \pm 0.40 \times 10^{14}$ atoms/cc STP (N=2)

The measured values (in November, 1999) were decay corrected to reflect the tritium concentrations on September 1, 1999. The uncertainties are estimates of random and systematic errors at a level of one standard deviation and N is the number of aliquots analyzed.

As mentioned previously, we have estimated that before the electrode was punctured, its free volume of ~ 0.6 cc contained about 5.7 mg $(H_2O+HOD+D_2O)_{l+g}$ and ($H_2+HD+D_2)_g$ at a total pressure of 18.8 atmospheres. Thus we calculate that the amounts of tritium inside the electrode before puncturing were:

In the H_2, HD and D_2, $T_g = 5.8 \pm 0.7 \times 10^{13}$ atoms

In the $H_2O+HOD+D_2O$, $T_l = 1.7 \pm 0.3 \times 10^{15}$ atoms

From which, $T_g/T_l = 0.03$, and total tritium is $T_t = 1.8 \pm 0.3 \times 10^{15}$ atoms

If we assume that the relative amounts of H and D in the various hydrogen and water species were approximately the same as found by the Finnigan analysis described previously, then we also find that $H_g/H_l = 0.6$ and $D_g/D_l = 0.3$.

During the time between sampling in the steel cylinder on September 1, 1999 and helium

isotope analysis at McM on September 19, 1999 we calculate that the ^{3}He production from tritium decay was $6.0\pm1.1\times10^{11}$ atoms/cc STP and therefore the ^{3}He concentration in the cylinder was $1.7 \pm 0.6\times10^{12}$ atoms/cc STP on September 1, 1999. The cylinder initially contained 1.09 cc STP gas on that date, which represented 2.7% of the gas phase sample in the electrode. Thus the electrode contained $6.9 \pm 2.4\times10^{13}$ atoms ^{3}He immediately before puncturing on September 1, 1999. We have estimated that the total tritium content in the electrode at this time was $1.8\pm0.3\times10^{15}$ atoms. If we assume that the ^{3}He was produced as a result of a single event injection of tritium, then it is easy to calculate that the event occurred 251 ± 100 days before September 1, 1999, or sometime between September 15, 1998 and April 3, 1999. This calculation indicates that the tritium was produced during cathodic or anodic electrolysis which lasted from October 31, 1998 to May 11, 1999 This result also indicates that tritium was not removed to large extent from the electrode interior during anodic electrolysis which lasted from February 17, 1999 until May 11, 1999. We believe that this was due to the fact that a very large fraction of the tritium was bound as HTO, DTO, and TTO and as such could not escape through the Pd wall into the electrolyte.

The Possibility of Contamination by Tritium and/or ^{3}He

Although every aspect of the sample handling and analysis at McM was checked carefully by performing many appropriate blank runs etc., we were acutely aware of the (remote) possibility that the large ^{3}He concentration found in the stainless steel sample cylinder was due to some sort of contamination. For a time we considered that this may have occurred during initial helium measurements at PNNL. Several procedural blanks were carried out with the PNNL mass spectrometer inlet system and these ruled out the possibility of contamination at this stage. In

addition, several other gas samples in similar containers and valves had been processed in the mass spectrometer inlet system at PNNL at the same time and in the same way as the D_2O electrode gas sample. Subsequent analyses of these samples at McM did not show any evidence of contamination by ^{3}He or tritium. For a time we entertained the possibility that contamination had been introduced in the Finnigan mass spectrometer inlet system when the electrode was punctured. The records were checked and showed that immediately before analyzing the samples from the H_2O and D_2O electrodes some blanks and a nitrogen calibration were performed to test the Finnigan system and no trace of tritium was observed. In addition, samples which were high in ^{3}He or tritium had not been processed in this system during several months prior to these experiments. As previously mentioned, a gas sample could not be collected from the H_2O electrode because the two sections of this electrode had not been welded. However, as will be described later, McM analyses of the Pd-black inside this electrode and in a section of the Pd wall did not show any unusual concentrations of ^{3}He similar to those observed for the D_2O electrode. We believe that these facts rule out the possibility of any significant contamination of tritium and/or ^{3}He in the Finnigan inlet system.

Further Helium Measurements in the Electrode Gas Sample

After the above McM analyses were completed, the remainder (0.75 cc STP) of the electrode gas sample was transferred by a mercury toepler pump to a new leak tested and helium blank tested stainless steel container with a new high vacuum valve which was then shipped to PNNL for further ^{3}He and ^{4}He analyses using the most sensitive technique wherein approx 60% of the helium in a gas aliquot is admitted to the mass spectrometer volume. Two aliquots were analyzed on December 19, 1999 and a third aliquot was analyzed on February 10, 2000. The results are given in Table III along

with the McM result of September 19, 1999 for comparison. The observed increase of ^{3}He with time clearly confirms the presence of tritium, although the actual rate of increase should be carefully examined.

Assuming the presence of ^{3}H$_0$ atoms of tritium at t = 0, the amount of radiogenic ^{3}He is given by ^{3}He$_r$ = ^{3}H$_0$(1-e$^{-\lambda t}$), where λ is the decay constant of ^{3}H (26), assuming that the system was closed with respect to ^{3}He and tritium. Thus a plot of ^{3}He$_r$ versus (1-e$^{-\lambda t}$) as shown in Figure 2 should yield a straight line. We have used the method of least-squares fitting of points with experimental uncertainties as given by York (27) to determine the best straight line fit and we find that the slope indicates a tritium content (on September 1, 1999) of $1.44\pm0.28\times10^{14}$ atoms/cc STP which is in reasonable agreement with the value of $2.06\pm0.40\times10^{14}$ atoms/cc STP found from the actual tritium measurements (via accumulated ^{3}He) on aliquots of the sample in the 41.6 cc steel container.

Total Production of Tritium

Our measurements indicate that the D$_2$O electrode contained $5.8\pm0.7\times10^{13}$ atoms T as HT, DT, and TT, and $1.7\pm0.3\times10^{15}$ atoms T as HTO, DTO, and TTO at the end of the anodic episode, assuming that no loss occurred between then and when the electrode was punctured. We have calculated that the gas pressure at that time was about 18.8 atm. in a free volume of 0.6 cc. Arata and Zhang have quoted a pressure of 1000 atm. attained in similar electrodes during electrolysis (28). For the purpose of illustration, we will assume that the gas pressure in our experiment was between 100 atm. and 1000 atm. at the end of cathodic electrolysis. Thus we calculate that at this stage the electrode contained between 0.31×10^{15} atoms and 3.1×10^{15} atoms T in the gas phase. We will also assume that the amount of T in the aqueous phase did not change significantly during the anodic

episode because during this time only gaseous hydrogen is removed from the interior of the electrode. Thus as a preliminary estimate, we conclude that the total production of tritium during cathodic electrolysis was between 2.0×10^{15} atoms and 4.8×10^{15} atoms, and that 81-98% of the T in the gas phase escaped from the electrode during the anodic electrolysis. It should be emphasized however that we do not know what pressure was reached in the electrode during normal electrolysis. The only reasonably hard number we have at present is the estimated pressure of ~ 18.8 atm. in the electrode before it was punctured.

Tritium in the Electrolyte

Before electrolysis began, the tritium content in the D_2O electrolyte was 50 ± 1 dpm/ml which is equivalent to $\sim 1.2 \times 10^{12}$ atoms in the 0.5 L electrolyte volume. After electrolysis was completed the tritium content was measured at 67 ± 1 dpm/ml, indicating that at least 4×10^{11} atoms tritium had entered the electrolyte and exchanged with D and H in D_2O and H_2O during the anodic phase. The actual amount was certainly larger than this because the cell was not well isolated from the atmosphere during electrolysis as shown by the fact that the H_2O concentration increased from $\sim 0.1\%$ at the beginning to $\sim 10\%$ at the end. The total amount of tritium increase measured in the electrolyte is only 0.7% of the gaseous tritium as HT, DT, and TT estimated to have remained in the electrode void at the end of the anodic phase of electrolysis. While the observed $\sim 30\%$ increase of tritium in the electrolyte appears small in this sense, it is worth noting that it constitutes the only statistically significant case in more than 500 similar assays of tritium associated with Pd cathodes and D_2O electrolysis performed at SRI.

^{3}He-^{4}He Measurements in the Pd-black and Al-foil

In a previous paper, Clarke ([16]) has described ^{3}He-^{4}He measurements in 2-6 mg samples of Pd-black provided by Professors Arata and Zhang from the interior volumes of Pd cathodes which had demonstrated excess heat during D_2O electrolysis in their laboratory. Similar ^{3}He-^{4}He measurements and techniques have also been described by Clarke and Clarke ([17]). These methods were used with minor modifications for the SRI Pd-black powders. The previous McM measurements ([16]) had showed that there were small and variable amounts of ^{3}He and ^{4}He in the Arata-Zhang Pd-black powders, which included one sample which had not been used in any electrolysis experiment. It should be noted however, that the amounts of ^{3}He and ^{4}He were factors of 10^6-10^9 lower than Arata and Zhang have observed in similar specimens of Pd-black ([10], [11], [12], [13], [14]).

During previous McM work, it was found that pieces of Al foil used to wrap the Pd-black samples also contained small and variable amounts of ^{3}He and ^{4}He ([16]). Before the Pd-black measurements described herein commenced it was decided to examine other samples of Al foil in the hope of finding a foil containing lower and less variable helium. To this end, a new roll was purchased from a local hardware store and a 1.0 cm^2 piece analyzed on August 4, 1999 was found to contain $570 \pm 32 \times 10^3$ atoms ^{3}He, at a concentration of $141 \pm 8 \times 10^3$ atoms/mg. This may be compared with the highest value of $1096 \pm 21 \times 10^3$ atoms/mg found previously([16]) for the Pd-black sample A-3. In a further search for a "better" Al foil, helium isotope analyses were carried out on seven pieces of Al foil which had been used in the small sample helium work of H.Farrar IV and B.M. Oliver since ca.1966 and found by them to contain especially low amounts of ^{4}He. The ^{3}He and

[4]He results obtained at McM are shown in Figures 3 and 4. It is apparent that in these respects, the Farrar-Oliver foil is superior to the foil used in the previous McM study (16). Although we do not pretend to understand fully the origin of these sporadic small amounts of anomalous [3]He and [4]He trapped in metals such as aluminum, we will use the average values as valid corrections for the Pd-black samples wrapped in such foil and vaporized on line to the mass spectrometer.

Another technical improvement as compared to the previous study (16) was effected near the end of the McM Pd-black measurements reported in this paper. A jacket cooled to liquid N_2 temperature was added to surround the pyrex glass sample container on line to the mass spectrometer. In this way, the "hot blank" of atmospheric helium due to radiant heating of the furnace wall by the W coil and heating due to condensation of vapor from the Al foil wrapping and the Pd samples was significantly reduced.

A summary of [3]He and [4]He measurements made at McM on Pd-black samples from the H_2O and D_2O electrodes is given in Table IV. Several features are immediately apparent:

(1). [4]He results for the samples of Pd-black from the D_2O electrode are in good agreement with the independent PNNL results (see Table II) and previous McM results (16), and as before, they do not confirm the very much higher concentrations found in similar specimens by Arata and Zhang.

(2). As mentioned above, improved (lower) "hot blanks" were secured for 94B (5) and 94 B (6). Accordingly, we believe that the weighted mean [4]He concentration of $0.22\pm0.05\times10^9$ atoms/mg for these two samples is a reliable indicator of [4]He in the Pd-black. However, because we cannot eliminate the possibility that the Pd-black contains a trace of trapped atmospheric helium, we believe that the above [4]He concentration should be regarded as a high upper limit for production of [4]He in the Pd-black during the D_2O electrolysis at SRI.

(3). ^{3}He results for Pd-black from the H_2O electrode are comparable to previous results for the specimen of Pd-black (D) which had not been used in any electrolysis experiment ([16]).

(4). ^{3}He results for Pd-black from the D_2O electrode appear to be anomalous in a similar sense to the ^{3}He results in the gas sample obtained by puncturing the electrode at PNNL. The data for the D_2O samples 94B (1) to 94B (4) analyzed during a few days at the end of November 1999 indicate that the ^{3}He concentration is very roughly constant but with definite variation beyond analytical uncertainty as if due to sample inhomogeneity. Samples 94B (5) and 94B (6) which were analyzed in February and March 2000 show clear evidence of enhancement of ^{3}He due to tritium decay.

As previously in the case of the electrode gas sample, we will assume a single event injection of $^3H_0$ atoms of tritium at t = 0, and that the system was closed with respect to ^{3}He and tritium. Figure 5 shows a plot of ^{3}He versus $(1-e^{-\lambda t})$. We have again used the method of least-squares fitting of points with experimental uncertainties as given by York ([27]) to determine the best straight line fit to the data and we find that the "zero time" i.e. the date when ^{3}He = 0, was July 30, 1999 with an estimated uncertainty of ± 12 days.

It is very puzzling that the least squares fit line extrapolates to ^{3}He = 0 on July 30, 1999 which is several months after the key date of May 11, 1999 which marked the end of anodic electrolysis, or January 29, 1999 when cathodic electrolysis was completed. It appears that the tritium responsible for the observed growth of ^{3}He in the D_2O Pd-black from the end of November 1999 to April 20, 2000 did not reside in the Pd particles for several months after its production. A possible explanation is that the tritium produced during electrolysis exchanged rapidly with H and D in H_2O or D_2O on the surfaces of the Pd particles in preference to residing as T inside the Pd

particles, and/or some factor such as the presence of Pd oxide on particle surfaces inhibited diffusion of tritium back into the Pd particles once it had escaped to the gas phase. In addition, although it may seem plausible to assume that the observed tritium was produced inside the Pd particles, this may not be the case. It is expected that further measurements which we are continuing, will shed some light on this problem.

^{3}He-^{4}He Measurements in Sections of the Pd electrodes

Two sections approx 0.8 mm thick were sliced from the center of each electrode at SRI and sent to McM for analysis. Small slices about 2 mm wide were cut from the H_2O and D_2O sections. First, a slice was cut out from the D_2O section with a steel knife and the slice was then chopped into two pieces with the knife. Then a slice was cut out from the H_2O section with a thin diamond saw and the slice was chopped into two pieces with another steel knife. Another slice was cut from the D_2O section with the diamond saw using a new blade and then this slice was chopped into four approx equal length pieces with a steel knife. After the analyses of these samples were completed, the remainder of the D_2O section was filed on the inner and outer edges with a coarse metal file and the chips were recovered to make two more samples. Weighing the chips and the section before and after filing allowed rough estimates of the thickness of Pd removed by filing. These were 0.10 ± 0.04 mm and 0.05 ± 0.02 mm for the outer and inner edges respectively. The ^{3}He-^{4}He results and descriptions of the locations of pieces are given in Table V.

It is apparent that the H_2O section does not show any credible evidence for excess ^{3}He or ^{4}He but the D_2O section shows very clear evidence for excess ^{3}He but essentially no evidence for excess ^{4}He. If we assume that the ^{3}He data for the four quarter pieces cut from the D_2O slice are

representative of the whole Pd electrode (mass ~ 78.7 g excluding the Pd-black), the total inventory of ^{3}He was approx 6.6×10^{10} atoms on or about February 5, 2000. At present, we do not have sufficient information to determine the actual concentration of the tritium parent or when it was injected into the wall of the electrode. However, the ^{3}He concentration gradient through the wall shown in Figure 6 clearly indicates that the source of tritium was inside the electrode or in the Pd-black, rather than inside the Pd wall. If we suppose that the tritium diffused through the Pd wall with a constant concentration at the inner surface, then the equation describing the steady-state concentration of tritium through the electrode wall is that for radial diffusion through the wall of a long cylinder given by Crank (29) which is

$$C = [C_1 \, Ln(b/r) + C_2 \, Ln(r/a)]/Ln(b/a)$$

where C_1 and C_2 are concentrations at the inner and outer surfaces, and a and b are inner and outer radii. In our electrode a = 3.5 mm and b = 7.0 mm so the above equation becomes

$$C = 2.81C_1 - 1.81C_2 - [(C_1 - C_2)/\, Ln(2)] \, Ln(r)$$

An equation of the form $C = A + B \, Ln(r)$ where A and B are constants determined by the boundary conditions should also be valid for ^{3}He produced in the wall from tritium decay provided that a steady-state condition is achieved for tritium and there is no diffusion loss of ^{3}He.

A logarithmic least squares fit to the ^{3}He data points shown in Table V and Figure 6 is given by

$$^3He = 6292 - 3219 \, Ln(r)$$

where ^{3}He is in units of 10^3 atoms/mg and r is in mm.

From this equation we obtain $C_1 = 2259 \times 10^3$ atoms/mg and $C_2 = 28 \times 10^3$ atoms/mg.

Stepwise Heating Experiment

A sample of 24.9 mg Pd-black from the D_2O electrode was placed in a thin wall Ni tube which had been outgassed under high vacuum overnight at approx $1000\ ^0C$. The Ni tube was placed in a stainless steel tube resistance furnace attached to the McM mass spectrometer inlet system. After calibration of the instrument with standard air aliquots and measurement of two inlet line blanks, the furnace temperature was raised in a series of steps from room temperature to $980\ ^0C$. Each temperature was held for 30 mins. and analysis of the helium isotopes released in one temperature step was completed before the gas in the next step was processed. The sequence of measurements was carried out in a continuous series on April 20, 2000. ^3He and ^4He results are given in Table VI and illustrated in Figures 7 and 8.

For the purpose of analysis we consider that the Pd-black is an assembly of uniform spheres of radius a. To obtain a solution, the following equation must be solved:

$$\partial C/\partial t = (D/r^2)\partial/\partial r(r^2\partial C/\partial r)$$

with the boundary conditions $C = C_0$ at $t = 0$ and $C = 0$, $r>a$ for $t \geq 0$

The solution given by Barrer (30) is:

$$C = -2C_0a/\pi r\sum(-1)^n/n\ \exp(-n^2\pi^2Dt/a^2)\sin n\pi r/a$$

Boyd et al. (31) have shown that

$$F = 1 - 6/\pi^2\sum(1/n^2)\exp(-n^2\pi^2Dt/a^2)$$

where F is the fraction diffused out of the sphere in time t. The above series has been numerically evaluated by Reichenberg (32) for values of F from 0.01 to 0.99. Table VI gives our experimental F values and the corresponding calculated values of Dt/a^2.

If the diffusion process can be described by an equation of the form $D = D_0 \exp(-U/kT)$ then

a plot of $Log(Dt/a^2)$ versus T^{-1} should give a straight line, and the slope should allow a calculation of the activation energy U. A graph of the ^{3}He data plotted in this way is shown in Figure 9. The first three low temperature points were omitted because evolved ^{3}He was at or below detection. The last three high temperature points were omitted because the ^{3}He release became approximately constant with increasing temperature. We opined that this was due to a sintering of the Pd-black which caused a sudden increase in effective particle radius. After the stepwise temperature series was completed, the Ni container was removed from the furnace and the Pd-black was examined with a low power microscope. The color had changed from black to light grey, and the Pd particles had indeed stuck together in a sinter.

It is apparent from Figure 9 that the diffusion process can be adequately described by an equation of the form $D = D_0 \exp(-U/kT)$ and that only one activation energy of 1.1 eV = 25,500 cal/mole exists. It is also apparent that the ^{3}He formed from tritium is quantitatively retained in the Pd-black at room temperature. If we use the approximation for diffusion from a sphere given by Booth (33), i.e. that $F = 6(Dt/\pi a^2)^{1/2}$ for $F \leq 0.1$, it is easy to show that the loss of ^{3}He due to diffusion is only about 6% per million years at 25 ^{0}C.

^{4}He Results

The weighted mean value for ^{4}He in the sample of gas released by puncturing the D_2O electrode is $4.0 \pm 0.9 \times 10^{11}$ atoms/ccSTP - see Table III. Thus the amount of ^{4}He in the cylinder when it was analysed at McM on September 19, 1999 was $3.9 \pm 0.9 \times 10^{11}$ atoms. As mentioned previously, after McM analyses were completed, the sample gas was transferred to a new stainless steel

container which was shipped to PNNL for further analysis. The original container was pumped out thoroughly and the valve was tightly closed. After 7 days, the cylinder was attached to the McM mass spectrometer, and helium isotopes were measured in the usual way. The results gave an upper limit of 1.2×10^8 atoms ^{4}He/day for leakage of atmospheric helium into the cylinder, which indicated that no more than 2.3×10^9 atoms ^{4}He could have leaked into the cylinder during the time between sample collection on September 1, 1999 and the McM analysis on September 19, 1999. However, the Finnigan measurements on September 1, 1999 showed that the sample cylinder contained 0.6% N_2 and 0.2% O_2. If these amounts are due to a previous air leak or a residue of air because of incomplete pumping of the electrode prior to welding, then the N_2 and O_2 should be accompanied by about 1.1×10^{12} atoms/cc STP ^{4}He, or more than that if the leak was fractionating with respect to ^{4}He versus N_2. This is more than enough to account for the observed ^{4}He in the cylinder.

As mentioned previously, we believe that the weighted mean value of 0.22×10^9 atoms/mg ^{4}He for Pd-black samples 94B (5) and 94B (6) (see Table IV) is a high upper limit for any production of ^{4}He in the Pd-black during D_2O electrolysis. The weighted mean ^{4}He value for the six electrode section samples processed using liquid N_2 cooling of the furnace envelope, 12261-96E (3) to 12261-96E (8), is $0.05 \pm 0.04 \times 10^9$ atoms/mg, where the uncertainty is twice the standard error. Although we do not know the original concentrations of ^{4}He in the Pd-black used or in the Pd electrode before electrolysis, it should be mentioned that we have recently measured amounts of ^{4}He from 0.03×10^9 to 0.06×10^9 atoms/mg in several specimens of ordinary Pd wire (Aithaca, 1.0 mm diam.). These amounts should be compared with literature values for ^{4}He in ordinary Pd wire using comparable laboratory equipment to that used in this work. Values of 0.008×10^9 atoms/mg and 0.026×10^9 atoms/mg were measured for two pieces of Pd wire (Johnson-Matthey, 1mm diam.) by Kurz [34]

and a value of $<0.010 \times 10^9$ atoms/mg was found during analyses of several pieces of Pd wire (Mathey-Bishop, 0.5mm diam.) by Lupton (34).

The ^{4}He data from the stepwise heating experiment (see Figure 8) indicate that ^{4}He is released from the Pd-black from about 400 ^{0}C to 980 ^{0}C, with a maximum at about 700 ^{0}C. The sum of all the ^{4}He released from room temperature to 980 ^{0}C from the 24.9 mg sample is $2.1 \pm 1.1 \times 10^9$ atoms which corresponds to $0.08 \pm 0.05 \times 10^9$ atoms/mg. The ^{4}He released from the Pd-black when the sample was removed from the furnace after the stepwise heating experiment and a portion was vaporized amounted to $0.15 \pm 0.01 \times 10^9$ atoms/mg. Thus total ^{4}He is $0.23 \pm 0.06 \times 10^9$ atoms/mg. This value is in good agreement with the weighted mean value of $0.22 \pm 0.05 \times 10^9$ atoms/mg for the Pd-black samples 94B (5) and 94B (6). Our measurements therefore indicate that there is indeed some ^{4}He trapped in the Pd-black after it was used in the D_2O electrolysis experiment. However, we consider that such a small amount of ^{4}He may be due to atmospheric helium present in microscopic bubbles of air or tank helium in cover gas used during manufacture of the Pd-black. To put the conclusion in another way, we see no compelling reason(s) to assume any other origin than the earth's atmosphere or crust for the small quantities of ^{4}He seen in our experiments.

Measurement of ^{4}He in a 0.1 mm layer filed from the outer edge of the section cut from the D_2O electrode gave a value of $-0.01 \pm 0.03 \times 10^9$ atoms/mg (see Table V). This value can be used to set a limit on near surface production of ^{4}He via the reaction $D + D = {}^4He + \gamma$. If we take the upper limit for near-surface ^{4}He to be 0.05×10^9 atoms/mg (two sigma) and the surface area of the electrode as 9.0 cm^2 then the inventory of ^{4}He in the 0.1 mm thick layer was no more than 5.5×10^{10} atoms. Because 50% of the total ^{4}He produced via classical D-D fusion would be expected to recoil into the Pd with a range < 0.1mm, and the other 50% into the electrolyte, 5.5×10^{10} atoms ^{4}He is also a valid

upper limit for the amount of ^{4}He that entered the D_2O electrolyte in our experiment during 90 days of cathodic electrolysis. This limit, expressed per unit time and per unit electrode area, is many orders of magnitude below the observed amounts of ^{4}He of 10^{14}-10^{15} atoms produced in 3.1 days of D_2O electrolysis for a Pd electrode area of 2.6 cm^2 as claimed by Miles et al. (35). Therefore it would appear that these observations require some other explanation than conventional D-D fusion near the Pd electrode surface.

Tritium versus Heat

We have estimated that the amount of tritium produced in the cathode was between 2.0×10^{15} atoms and 4.8×10^{15} atoms. If we assume that the tritium was produced by the reaction $D + D = {}^3H + {}^1H + 4.03$ MeV, then the total released energy was between 1.3 KJ and 3.1 KJ. These numbers should be compared with the excess energy of 64 ± 6 MJ measured at SRI (18) and the value of ~ 100 MJ indicated by Arata and Zhang (11) for similar cathodes and D_2O electrolysis times as in our experiment. Clearly, if ^3H is produced within the cathode void by the above nuclear reaction, it does not contribute significantly to the observed excess heat. If there are any other products of D-D fusion (such as ^3He and ^4He) associated with the observed heat production, they must be generated and released at the cathode surface in such a way that practically none of the products recoil into the Pd.

CONCLUSIONS

(1). During electrolysis of an Arata-style electrode in D_2O for 90 days as a cathode and 83 days as an anode, at least 1.8×10^{15} atoms of tritium were generated inside the electrode and the

estimated pressure was ~ 18.8 atm. at the end of anodic electrolysis. If the internal pressure was 100-1000 atm., the total production of tritium was between 2.0×10^{15} atoms and 4.8×10^{15} atoms.

(2). Estimates of tritium and ^{3}He inside the electrode at the time it was punctured indicate that if the tritium was injected in a single event, this occurred sometime during cathodic or subsequent anodic electrolysis.

(3). There is definite evidence of excess ^{3}He from tritium decay in all samples of Pd-black from the D_2O electrode whereas three samples of Pd-black from the H_2O electrode show lower and variable ^{3}He similar to previous McM results for Pd-black ([17]). Analysis of the D_2O Pd-black data indicates that the tritium parent of ^{3}He was not introduced into the interior of the particles until several months after electrolysis was completed.

(4). Measurements of the ^{3}He concentration gradient through the 0.35 mm wall of the D_2O electrode clearly indicate that the ^{3}He is the decay product of tritium which diffused from a source inside the electrode. Further measurements are needed to determine when the tritium was injected and how much remains at present.

(5). There is no evidence for any significant production of ^{4}He either in the gas phase sample from the D_2O electrode, the Pd- black inside the two electrodes, or in pieces of Pd cut from sections of the electrodes and thin samples scraped from the inner and outer surfaces. The upper limits found for ^{4}He in Pd-black are many orders of magnitude below corresponding values published by Arata and Zhang ([10], [11], [12], [13], [14], [15]) who used identical electrodes and D_2O electrolysis for similar times. The upper limit for ^{4}He production near the electrode surface (assuming conventional D-D fusion and recoil of 50% of the ^{4}He into the electrode) is many orders of magnitude lower than observed amounts of ^{4}He evolved during D_2O electrolysis using Pd electrodes by Miles et al. ([35])

(6). A stepwise heating experiment from room temperature to 980 ^{0}C was carried out on line to the McM mass spectrometer using 24.9 mg of the Pd-black which had been inside the Pd electrode during D_2O electrolysis. The results showed that the diffusion process for trapped ^{3}He can be described by an equation of the form $D = D_0\exp(-U/kT)$ where $U = 1.1$ eV, and that loss of trapped ^{3}He due to diffusion is only about 6% per million years at 25 ^{0}C.

(7). These experiments have suggested many avenues of investigation which should be explored in order to achieve a detailed understanding of the observed effects.

ACKNOWLEDGEMENTS

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TABLE 1

PNNL (Finnigan) Analysis of Electrode (D_2O) Interior Gas

Species	Percentage of total
H_2	13.2
HD	8.9
D_2	2.3
H_2O	24.6
HOD	35.5
D_2O	14.4
N_2	0.6
O_2	0.2
N_2O	0.1

TABLE II

PNNL Measurements of ^{3}He and ^{4}He in Pd-black from Arata-style Pd Cathodes

Sample[a]	Mass, mg	^{4}He Atoms/mg[b] $(\times 10^9)$	^{3}He Atoms/mg[b] $(\times 10^6)$
94A (a)	17.39	0.03 ± 0.13	-23 ± 52
94A (b)	13.50	0.23 ± 0.17	67 ± 67
94B (a)	15.09	0.15 ± 0.15	60 ± 60
94B (b)	13.36	-0.04 ± 0.17	37 ± 67
	Weighted Mean[c]	0.09 ± 0.12	35 ± 45

[a]All samples were analysed on September 12, 1999. 94A and 94B samples were from the H_2O and D_2O electrodes respectively.

[b]Uncertainties are estimates of random and systematic errors at a level of one standard deviation. They do not include the effect of sample inhomogeneity.

[c]Uncertainties for weighted means are twice the standard error.

TABLE III

^{3}He and ^{4}He in Electrode (D$_2$O) Gas Sample

Analysis Date - Laboratory	^{4}He Atoms/cc STP[a] $(\times 10^{11})$	^{3}He Atoms/cc STP[a] $(\times 10^{12})$
Sept. 19, 1999 - McM	2.5 ± 0.7	2.3 ± 0.5
Dec. 18, 1999 - PNNL	3.6 ± 1.0	3.52 ± 0.18
Dec. 18, 1999 - PNNL	4.1 ± 0.6	3.71 ± 0.19
Feb. 10, 2000 - PNNL	4.3 ± 0.3	5.35 ± 0.27

[a]Uncertainties are estimates of random and systematic components at a level of one standard deviation. In most cases, pressure measurements were the major source of error.

TABLE IV

McM Measurements of ^{3}He and ^{4}He in Pd-black from Arata-style Pd Cathodes

Sample[a]	Analysis Date[b]	Mass, mg	^{4}He Atoms/mg[c] ($\times 10^9$)	^{3}He Atoms/mg[c] ($\times 10^3$)
94A (1)	Nov. 20, 1999	0.72	-0.3 ± 2.2	481 ± 68
94A (2)	Nov. 29, 1999	2.14	1.0 ± 0.7	-34 ± 35
94A (3)	Dec. 02, 1999	1.97	1.2 ± 0.8	15 ± 44
94B (1)	Nov. 20, 1999	1.51	2.6 ± 1.0	4781 ± 64
94B (2)	Nov. 25, 1999	2.59	0.4 ± 0.6	4288 ± 41
94B (3)	Nov. 28, 1999	7.82	-0.13 ± 0.19	4198 ± 24
94B (4)	Nov. 29, 1999	4.27	-0.10 ± 0.36	5023 ± 38
94B (5)	Feb. 29, 2000	1.46	0.31 ± 0.13	7734 ± 97
94B (6)	Mar. 15, 2000	3.55	0.21 ± 0.03	8341 ± 41

[a]94A and 94B samples were from the H_2O and D_2O electrodes respectively.

[b]After Feb. 2, 2000, samples were treated in the improved vacuum chamber with liquid N_2 cooling. See the text.

[c]Uncertainties are estimates of random and systematic errors at a level of one standard deviation. They do not include the effect of sample inhomogeneity.

TABLE V

McM Measurements of ^{3}He and ^{4}He in Sections from the Arata-style Pd Cathodes

Sample[a]	Analysis Date	Mass, mg	^{4}He Atoms/mg[b] ($\times 10^9$)	^{3}He Atoms/mg[b] ($\times 10^3$)
12261-96B (1)	Jan. 21, 2000	4.18	0.32 ± 0.14	16 ± 15
12261-96B (2)	Jan. 23, 2000	3.43	0.28 ± 0.12	-25 ± 23
12261-96E (1)	Jan.15, 2000	5.57	0.25 ± 0.20	467 ± 16
12261-96E (2)	Jan.16, 2000	2.99	0.23 ± 0.20	1532 ± 32
12261-96E (3)	Feb. 3, 2000	6.91	0.04 ± 0.03	261 ± 9
12261-96E (4)	Feb. 5, 2000	7.72	0.10 ± 0.03	486 ± 9
12261-96E (5)	Feb. 6, 2000	6.62	0.04 ± 0.03	1061 ± 11
12261-96E (6)	Feb. 7, 2000	5.36	0.11 ± 0.04	1563 ± 21
12261-96E (7)	Feb. 10, 2000	10.43	-0.01 ± 0.03	307 ± 10
12261-96E (8)	Feb. 13, 2000	4.22	-0.04 ± 0.05	2656 ± 30

[a]12261-96B and 12261-96E sections shaped like ordinary metal washers were cut from the H_2O and D_2O electrodes respectively. Samples labeled (1) and (2) were outer and inner half (approx) pieces chopped from 2 mm wide slices cut from the sections. Samples labeled (3) to (6) were quarter (approx) pieces from outside to inside. Samples labeled (7) and (8) were obtained from filings scraped from the outside and inside edges of the D_2O section – see the text.

[b]Stated uncertainties are estimates of random and systematic errors at a level of one standard deviation.

TABLE VI

^{3}He and ^{4}He Evolved From 24.9 mg Pd-black (D_2O electrode) as a Function of Temperature

Temperature ^0C	^{4}He Atoms ($\times 10^9$)	^{3}He Atoms ($\times 10^3$)	$\sum{}^3$He Atoms ($\times 10^3$)	F	Dt/a^2
25	0.11 ± 0.08	15 ± 29	15	0.00006	-----------
35	-0.05 ± 0.08	-5 ± 23	11	0.00004	-----------
45	-0.20 ± 0.08	-12 ± 29	-2	-0.00001	-----------
70	0.20 ± 0.08	0 ± 30	-2	-0.00001	5.37×10^{-12}
105	0.03 ± 0.08	7 ± 32	5	0.00002	2.93×10^{-11}
150	0.00 ± 0.08	73 ± 27	78	0.0003	8.10×10^{-9}
190	-0.19 ± 0.08	513 ± 61	591	0.002	4.67×10^{-7}
240	0.02 ± 0.08	776 ± 66	1368	0.005	2.50×10^{-6}
295	0.03 ± 0.08	2105 ± 89	3473	0.014	1.62×10^{-5}
360	0.00 ± 0.08	5500 ± 84	8973	0.035	1.09×10^{-4}
425	0.27 ± 0.08	17082 ± 129	26054	0.102	9.57×10^{-4}
490	0.12 ± 0.08	68205 ± 251	94260	0.368	1.49×10^{-2}
555	0.39 ± 0.08	49839 ± 218	144099	0.563	4.11×10^{-2}
620	0.31 ± 0.08	37095 ± 168	181194	0.708	7.70×10^{-2}
690	0.22 ± 0.08	15287 ± 159	196481	0.768	9.89×10^{-2}
755	0.50 ± 0.08	4431 ± 81	200912	0.785	1.07×10^{-1}
870	0.23 ± 0.08	5137 ± 95	206050	0.805	1.16×10^{-1}
915	-0.05 ± 0.08	4150 ± 79	210200	0.822	1.25×10^{-1}
980	0.11 ± 0.08 $(2.06 \pm 1.14)^a$	4248 ± 80	214448	0.838	1.33×10^{-1}
Reheat[b]	3.77 ± 0.25	41395 ± 270	255843	1.000	

[a]Total ^{4}He released from room temperature to 980 ^0C

[b]After the stepwise temperature experiment was completed, a portion of the Pd-black was vaporized to determine the total inventories of ^{3}He and ^{4}He – see the text.

FIGURE CAPTIONS

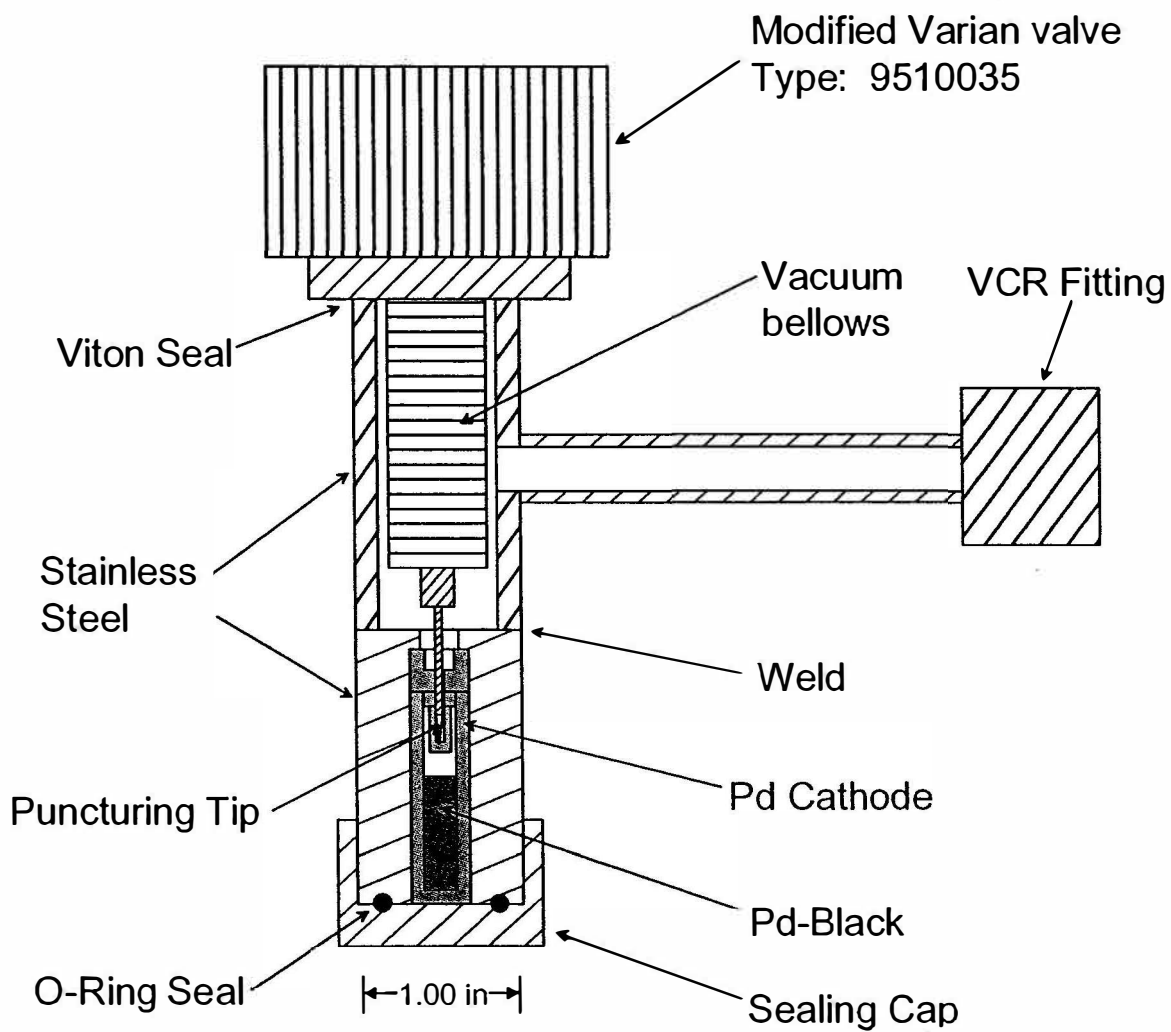Figure 1. Pd Electrode Gas Extraction Device used at PNNL.

Figure 2. ^{3}He concentration versus $(1-e^{-\lambda t})$ for aliquots of the sample of electrode gas collected on September 1, 1999 at PNNL. The line is a least-squares fit, and zero time is September 1, 1999.
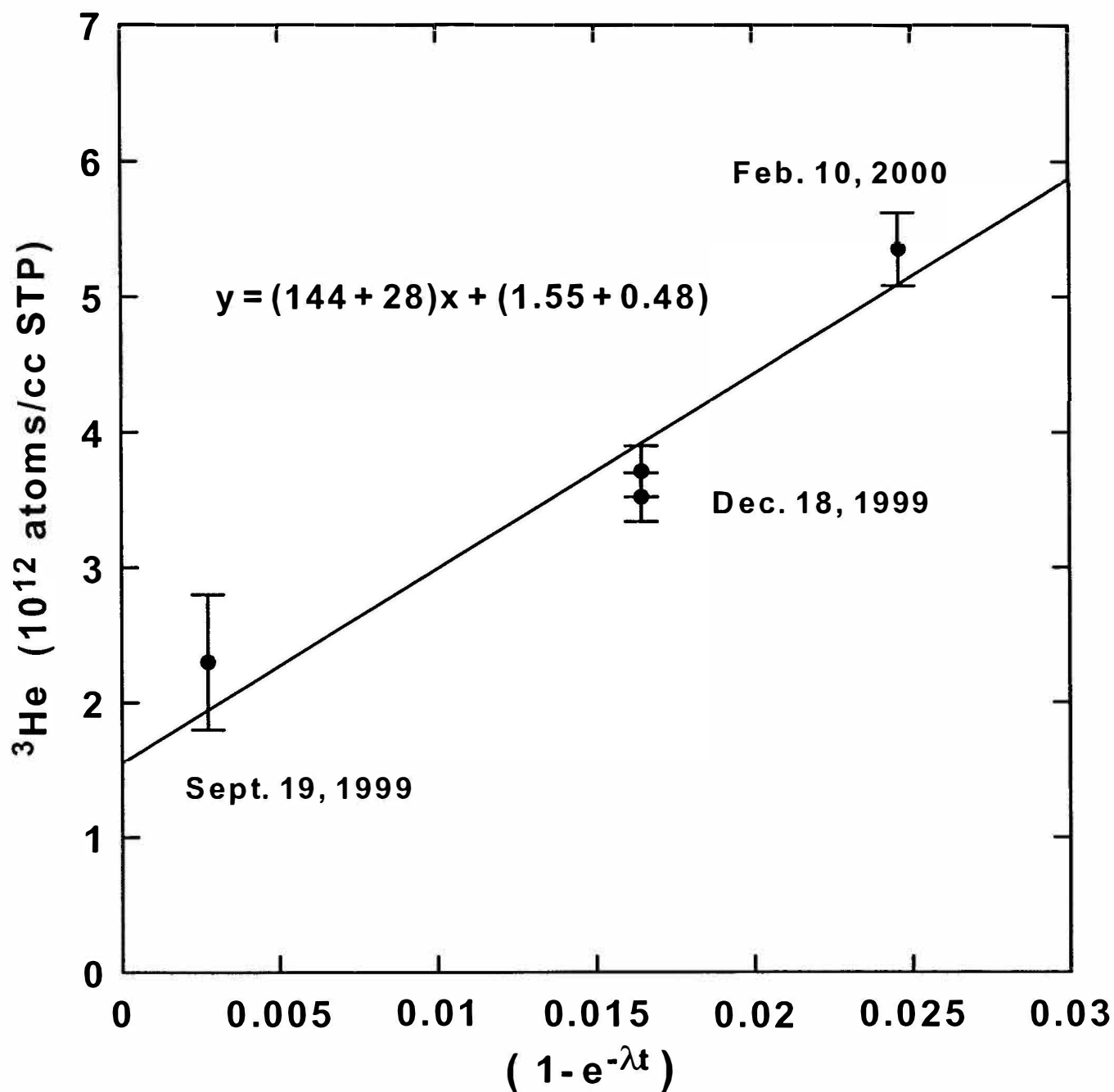
Figure 3. ^{4}He measured in seven pieces of Farrar-Oliver Al foil at McM- see the text. The ^{4}He intercept of 0.70×10^9 atoms represents a constant amount of atmospheric ^{4}He released from the inside of the furnace wall due to radiant heating by the hot W furnace coil. These measurements were carried out before the liquid N_2 jacket was installed on the furnace.

Figure 4. ^{3}He and ^{4}He concentrations in seven pieces of Farrar-Oliver Al foil.

Figure 5. ^{3}He versus $(1-e^{-\lambda t})$ for 2-8 mg samples of Pd-black from inside the Pd electrode used during D_2O electrolysis. Also included is the total ^{3}He result obtained in the stepwise heating experiment on April 20, 2000, and the subsequent vaporization of a part of the sample. The least squares fit line is drawn through (0,0) with zero time determined to be July 30, 1999 ($\pm$ 12 days) – see the text.

Figure 6. ^{3}He concentrations through the wall of the Pd electrode used during D_2O electrolysis as

determined from analyses of pieces cut from a 0.8 mm thick section from the middle of the electrode. The line drawn through the points is a least squares logarithmic fit – see the text.

Figure 7. Release of ^{3}He from Pd-black used during D_2O electrolysis as a function of temperature.

Figure 8. Release of ^{4}He from Pd-black used during D_2O electrolysis as a function of temperature. The curve has been drawn by eye through the points to indicate the apparent release of trapped ^{4}He from 500 ^{0}C to 980 ^{0}C.

Figure 9. The relationship between the diffusion coefficient D and 1/T for ^{3}He in the Pd-black used during D_2O electrolysis. The activation energy is 1.1 eV = 25,500 cal/mole.

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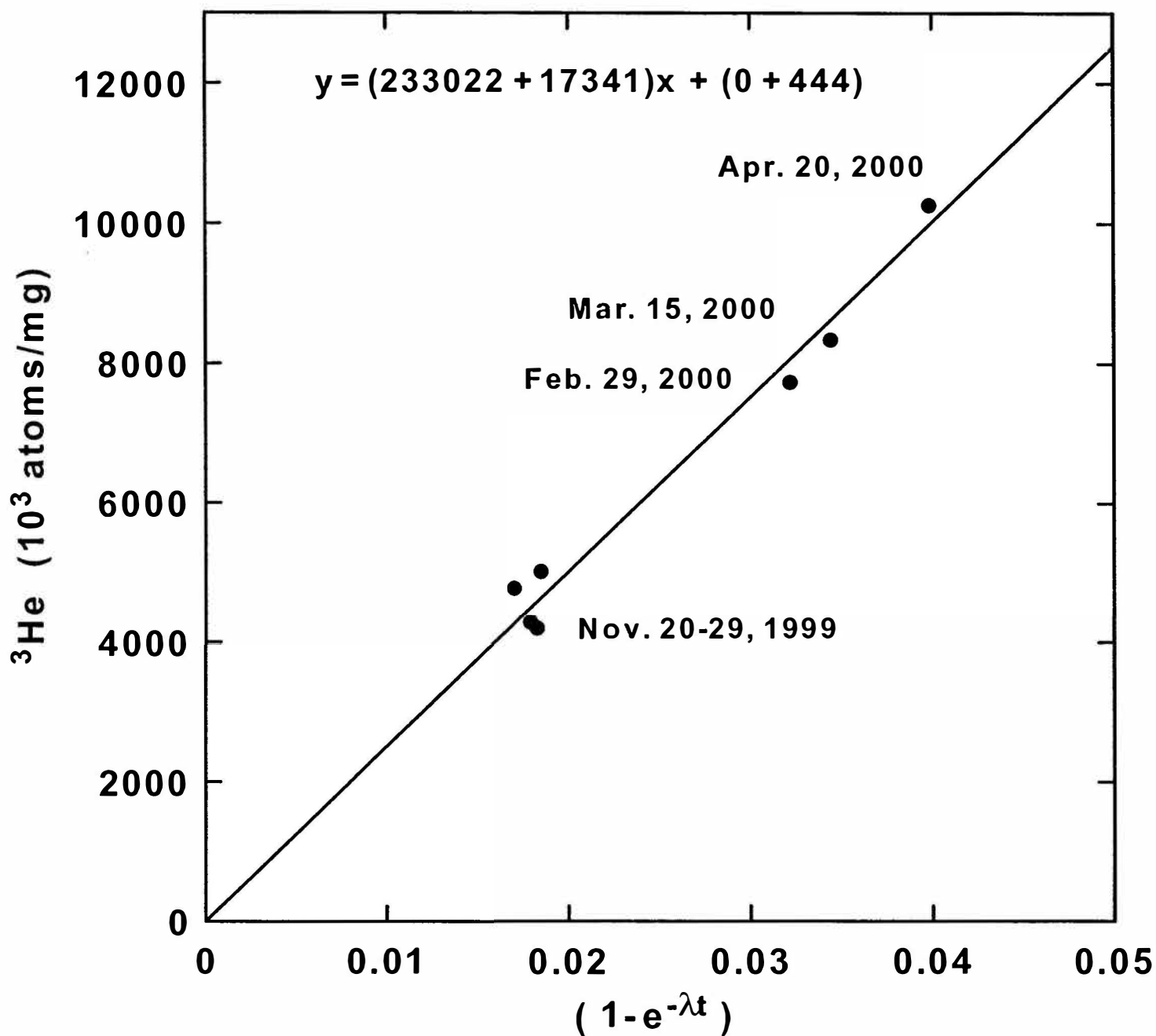
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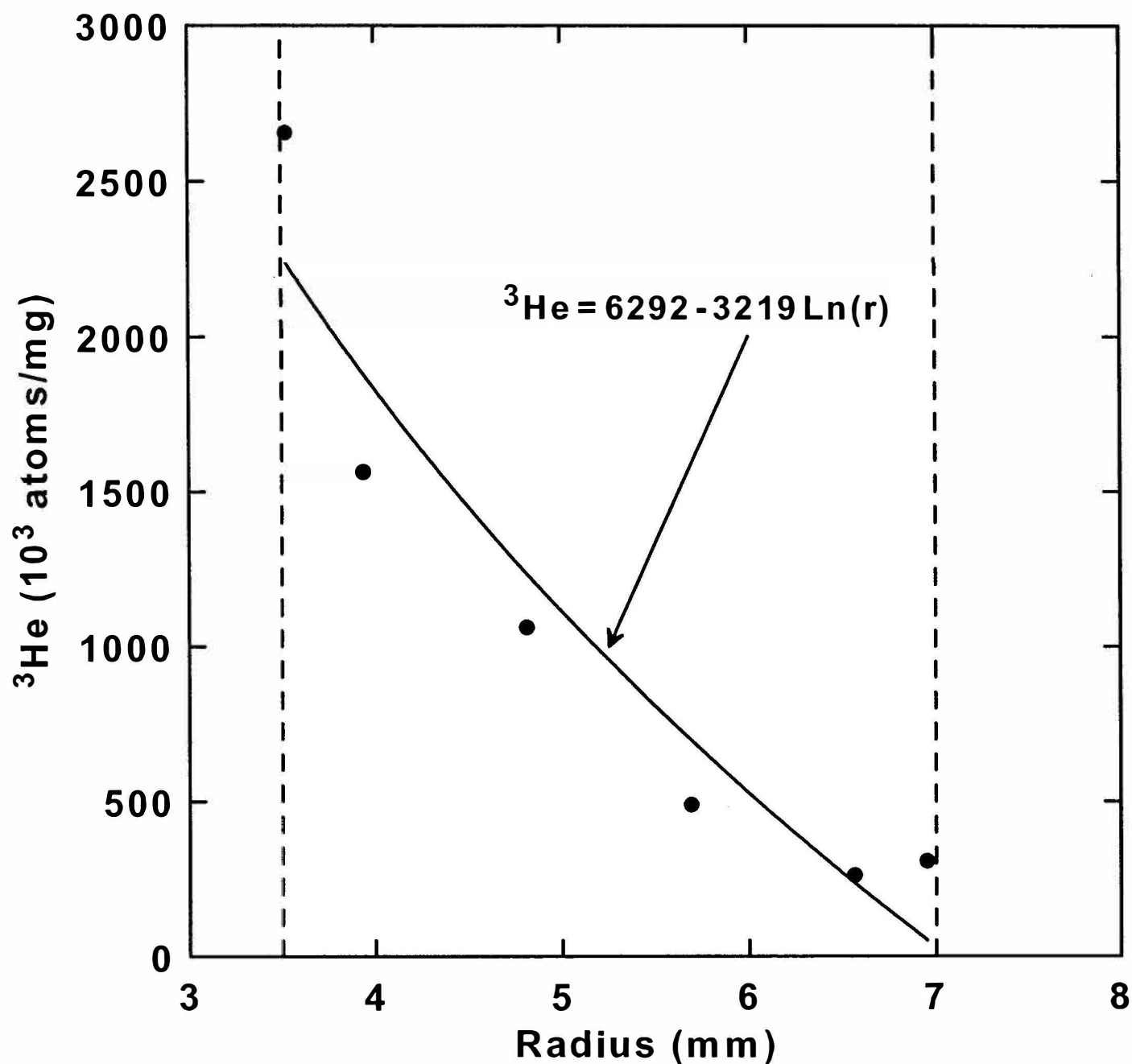

$$^3He = 6292 - 3219\,Ln(r)$$

Y-axis: ^{3}He (10^3 atoms/mg)

X-axis: Radius (mm)

Figure 7. Release of ^{3}He from Pd-black used during D_2O electrolysis as a function of temperature.
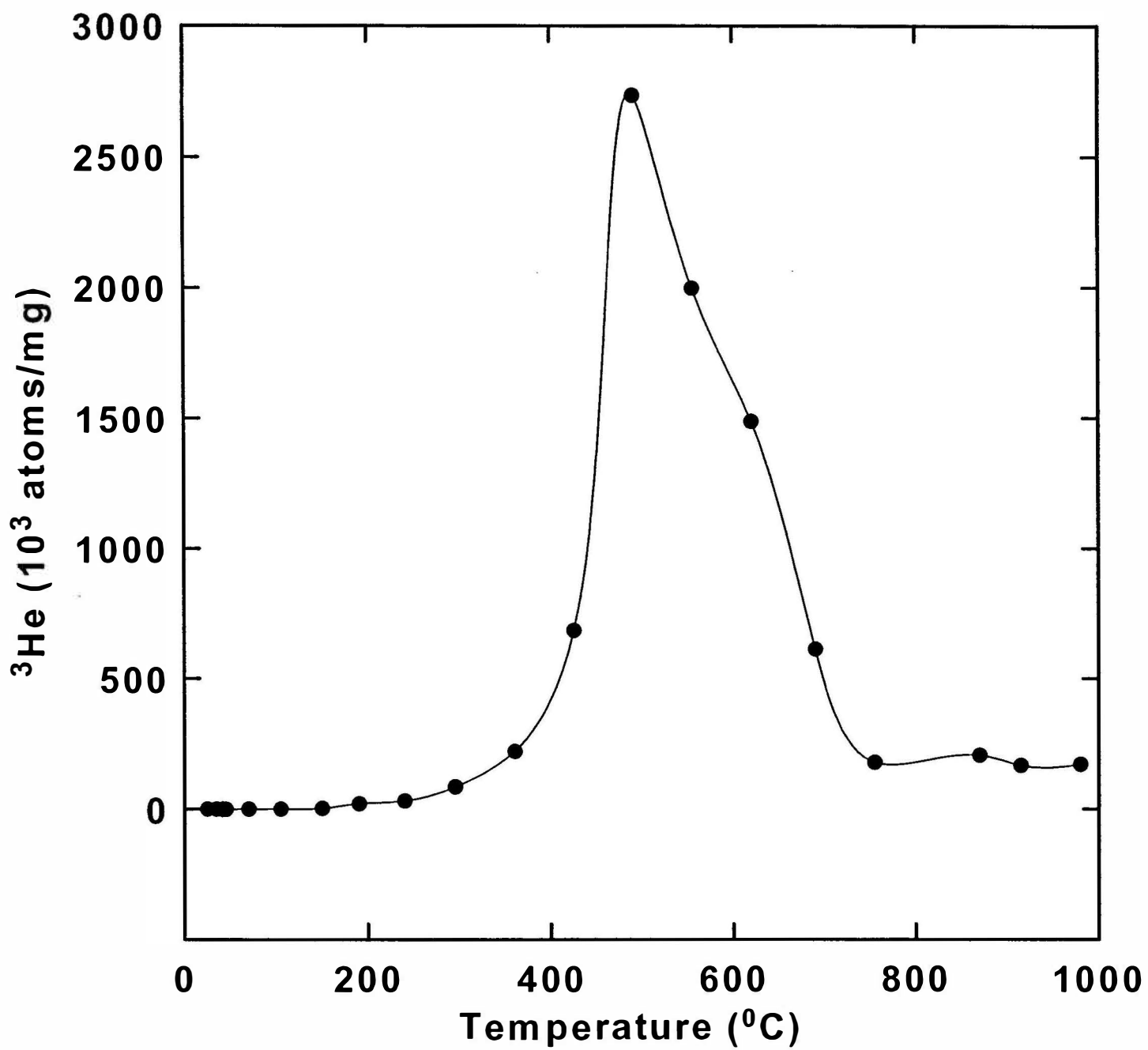
Figure 8. Release of ^{4}He from Pd-black used during D_2O electrolysis as a function of temperature. The curve has been drawn by eye through the points to indicate the apparent release of trapped ^{4}He from 500 ^{0}C to 980 ^{0}C.
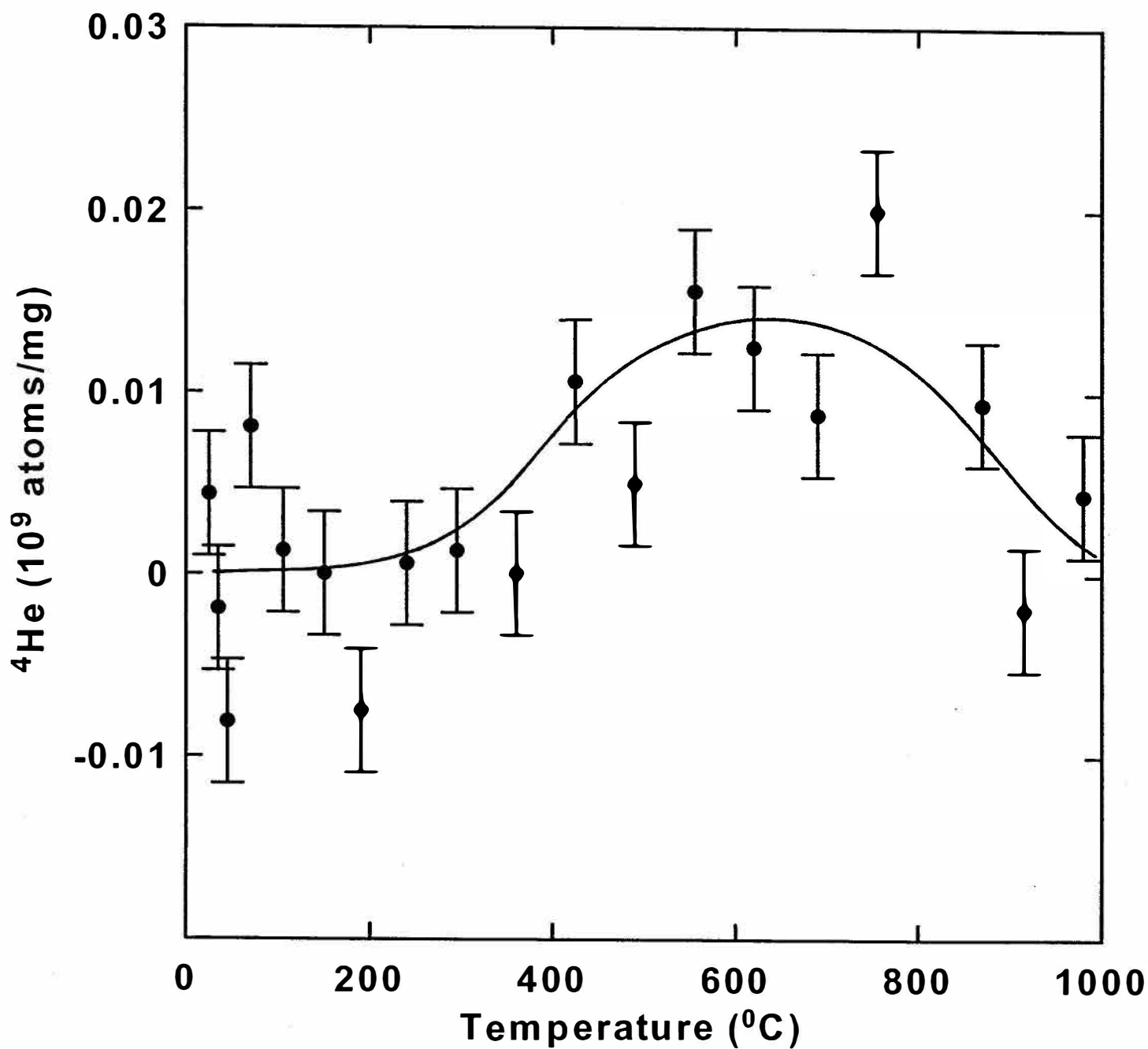
Figure 9. The relationship between the diffusion coefficient D and 1/T for ^{3}He in the Pd-black used during D_2O electrolysis. The activation energy is 1.1 eV = 25,500 cal/mole.

$y = -5.62x + 5.09$

Log Dt/a^2

1000/T[K]