PRODUCTION OF ^{4}He IN D_2-LOADED PALLADIUM-CARBON CATALYST I

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A series of lead vials of internal volume 1.0 cm^3 were charged with ~200 mg of carbon catalyst containing 0.5% Pd and 0.4% Pd. The vials were clamped to stainless steel manifolds on a vacuum line, then pumped out and filled with high-purity H_2 or D_2 at a pressure of 152 cm Hg and a temperature of 23°C. Several vials contained ordinary activated carbon instead of palladium-carbon, and some vials contained only H_2 or D_2. All the vials were stored in a sandbox heated to ~200°C for times up to 45 days before mass spectrometer measurements of ^{3}He and ^{4}He were made. No evidence was found for the high concentrations of ^{4}He claimed in similar experiments by several other researchers. The upper limit for the concentration excess of ^{4}He in D_2 in vials containing palladium-carbon is 11 ppt (parts per trillion) at the 95% confidence level. This limit for ^{4}He may be compared with previous claims in similar experiments of 100 ppm (parts per million) by Case and 11 ppm by George and McKubre et al.

KEYWORDS: *palladium-carbon catalyst, helium isotopes*

I. INTRODUCTION

In 1997, Case published an international patent application[1] which described production of heat and ^{4}He when a palladium-carbon catalyst was exposed to D_2 gas in a closed steel container at modest pressures, from a partial vacuum to 10 atm, and at temperatures from 150 to 250°C. Case restated his claims in 1998 (Ref. 2), citing reaction temperatures of 130 to 275°C, and noting that he had examined "many such catalysts, and found that a platinum-group metal supported on activated carbon, and a loading of about $\frac{1}{2}$ to 1% on the substrate seemed to be preferred." Case further stated that the D_2 from long-term runs had been analyzed by mass spectrometer and shown "to contain very roughly about 100 ppm of helium-4, which was not present in the research-grade D_2 fuel." This finding and the apparent excess temperature detected in D_2-loaded versus H_2-loaded containers led Case to conclude that the reaction $D + D = {}^4He + 23.8$ MeV was responsible.

Soon after the initial report[1] of Case's findings, George[3] set up similar experiments at SRI International (SRI). A 50-cm^3 stainless steel container containing ~10 g palladium-carbon catalyst was pumped out and subjected to the cleaning procedure described by Case[1] before filling it with D_2. The container was attached to a quadrupole-type mass spectrometer capable of resolving D_2 from ^{4}He (resolution ~ one part in 200) and 15 aliquots of the D_2 were assayed for ^{4}He over a period of 27 days. George's results were indeed remarkable: the ^{4}He concentration showed an approximately linear increase from <0.5 ppm after about four days to 11 ppm at 27 days, whereas 14 aliquots of H_2 taken from an identical container containing palladium-carbon under similar pressure and temperature conditions and over the same time interval showed no apparent increase of ^{4}He concentration above 0.4 ppm.

Recently, McKubre et al. have published a further account of the "Case replication" experiments at SRI (Ref. 4). The ^{4}He results described by George[3] were extended to 34 days, two other D_2 runs were reported, and further measurements from identical containers loaded with H_2 instead of D_2 were in good accord with George's results except for an unexplained increase of ^{4}He concentration in a H_2-loaded container from 1 to 2 ppm during the time period 20 to 41 days. McKubre et al. also placed temperature sensors in the catalyst, in the gas inside the containers, and in the air outside the containers. Thus, they were able to estimate the total excess energy from the D_2-loaded versus H_2-loaded containers at 150 KJ during a heating time of 20 days. The data indicated Q-values of 31 ± 13 and 32 ± 13 MeV per ^{4}He atom produced during the 20 days. It will be noted

*We are sorry to inform our readers that Dr. W. Brian Clarke is deceased.

that these Q-values are in excellent agreement with the known value of 23.8 MeV for the nuclear fusion reaction $D + D = {}^4He + \gamma$.

The SRI experiments were carried out with 50 cm^3 stainless steel vials containing ~10g palladium-carbon. The estimate of 32 ± 13 MeV per ^{4}He atom was deduced from the linear relationship between ^{4}He release and excess energy. Thus, the production of ^{4}He in an SRI container in 20 days must have amounted to $3.0 \pm 1.3 \times 10^{16}$ atoms ^{4}He. Because the measured concentration of ^{4}He at 20 days was 8 ppm, it follows that the D_2 pressure must have been constant at ~3 atm at 20°C or ~5 atm at 200°C, during the 20 days, assuming that the ^{4}He concentrations quoted by McKubre et al. are expressed in the normal way, i.e., as measured fractions of ^{4}He atoms to D_2 molecules in actual aliquots of the gas phase. As will be discussed later, although the initial D_2 pressure may indeed have been ~3 atm at 20°C, absorption by the palladium-carbon surely caused a rapid (within ~2 days) decrease in pressure to ~20% of the initial value. It does not seem plausible that the initial D_2 pressure of ~3 atm was maintained by periodic or continuous additions of D_2 from a tank because this would have resulted in a large systematic error due to spurious additions of ^{4}He from that source. Therefore, it is concluded that the ^{4}He concentrations quoted by McKubre et al. refer to the total initial D_2 (absorbed plus gas phase) in the containers.

It should be mentioned that the Case-SRI heat results have not been confirmed. Little[5] in a series of experiments with palladium-carbon loaded with D_2, under similar conditions as outlined by Case,[1,2] was unable to find any evidence for excess heat. Because of the apparent discrepancy, and the interest of some researchers in the possibility of low-temperature nuclear reactions, it was considered worthwhile to check the previous ^{4}He results using state-of-the-art mass-spectrometric techniques.

II. EXPERIMENTAL METHODS

II.A. Samples

Three palladium-carbon samples were donated by M. C. H. McKubre and F. L. Tanzella. Two of these contained 0.5% Pd and one contained 0.4% Pd. Aliquots of all three samples had previously shown apparent excess ^{4}He in D_2-loading experiments at SRI. One palladium-carbon sample containing 0.5% Pd was donated by K. L. Shanahan. The carbon used in this work was ordinary "activated" coconut charcoal, which had been used for many years in this laboratory to condense and separate inert gases. Deuterium and hydrogen gas were made by reacting heavy water and distilled water with granulated zinc at 400°C as described by Kirshenbaum.[6] The heavy water was made by distillation at Oak Ridge, Tennessee, in 1946, several years before atmospheric thermonuclear testing began, and consequently had a much lower tritium content ($T/D = 0.9 \pm 0.1 \times 10^{-15}$) than present-day heavy water. The distilled water had a T/H ratio of $3.0 \pm 0.2 \times 10^{-17}$. Production of ^{3}He via tritium decay was negligible for the decay times employed in these experiments.

II.B. Lead Tube Containers and Vacuum Techniques

Palladium-carbon and carbon samples weighing 0.19 to 0.21 g were placed in 8-cm lengths of 99.99% lead tubing (outer diameter = 0.95 cm, wall thickness = 0.16 cm), which were pinch-sealed at one end. About 10 cm of stainless steel ribbon (0.5 mm × 0.03 mm) was crumpled loosely and placed on top of the palladium-carbon and carbon to prevent the particles from jumping when pumping was started. It is considered that the steel ribbon did not interfere significantly with free flow of H_2 or D_2 in the containers. The lead tube technique for storing gas samples was developed in this laboratory for another purpose,[7] and extensive tests have shown that the vials have excellent integrity for outward leakage of sample helium or inward leakage of atmospheric helium. For example, mass spectrometer analyses of residual gas inside lead tube vials of internal volume ~1.0 cm^3, pumped out and sealed then stored in air at temperatures from 20 to 250°C for times of up to 2 yr show an accumulation of $<2 \times 10^8$ atoms ^{4}He.

The lead tube vials were attached with clamps to sidearms of two stainless steel manifolds on a vacuum line. Vials containing palladium-carbon and carbon were interspersed with empty vials on the manifold. All vials were heated to ~130°C with electrical heating tapes for 4 days, until the pressure reached 10^{-8} torr; H_2 and D_2 gas was made in a separate vacuum system and stored in 1-L Pyrex glass containers. The H_2 and D_2 were "cleaned" of traces of atmospheric helium by briefly pumping through a trap containing activated charcoal held at −196°C, then allowed to heat up to −120°C immediately before admitting the purified H_2 or D_2 to the manifold sections of the vacuum line. The procedure outlined by Case[1] was followed, i.e., the manifold sections were initially filled with H_2 or D_2 at a pressure of 152 cm Hg with the vials heated to 150°C, then allowed to stand for 1 h before pumping out. This procedure was carried out twice before filling the vials with H_2 or D_2 at a pressure of 152 cm Hg and a temperature of 23°C. Pinch-sealing of individual lead vials was done as rapidly as possible, within ~10 min. Twenty lead vials were filled with D_2 in one manifold, and 2 h later, 24 lead vials were filled with H_2 in the other manifold. Immediately after pinch-sealing, the vials were placed upright, with the palladium-carbon or carbon at the bottom, in a sandbox on a hot plate. Tests made with a temperature probe showed that there was a gradient from 200°C at the bottom of the lead vials to 190°C at the top.

II.C. Mass Spectrometry

The mass spectrometer was designed specifically for ^3He and ^4He measurements on small helium samples. The detection limits are $\sim 10^4$ and 10^8 atoms for ^3He and ^4He, respectively. The instrument is operated in the static mode, with simultaneous detection of ^3He and ^4He ion currents and a mass resolution of 1 part in 620. More detailed descriptions have been given in previous papers.[8–11] After removal from the sandbox, the lead-tube vials were each placed in a simple vacuum bellows puncturing device attached to the mass spectrometer inlet system. Helium samples prepared from 0.008 cm^3 STP air aliquots were used to calibrate the mass spectrometer during each series of analyses of ^3He and ^4He in H_2 or D_2 contained in the lead-tube vials.

III. RESULTS AND DISCUSSION

III.A. The ^3He and ^4He in the Palladium-Carbon

Before the work on H_2 or D_2-loading began, trapped helium was released from small pieces of the three SRI palladium-carbon samples by heating to 2300°C in the mass spectrometer inlet line as described previously.[9–11] The helium isotope results are given in Table I. It seems likely that the observed amounts are due to traces of atmospheric helium trapped in closed pores in the carbon and therefore not removed by pumping for ~12 h at 23°C in the mass spectrometer inlet system before analysis. The "worst case" example appears to be G75-E (A) which contains $0.73 \pm 0.09 \times 10^9$ of ^4He atoms/mg. It will be assumed that the 50 cm^3 containers used at SRI (Refs. 3 and 4) were charged with 10 g palladium-carbon with a true density of 2.0 g/cm^3 (Refs. 12 and 13). It is also assumed that in the SRI experiments the initial pressure of H_2 or D_2 was ~3 atm at 20°C (i.e., ~5 atm at 210°C) and that the ^4He concentrations[3,4] refer to the initial filling pressure of H_2 or D_2 in the container and not to the actual pressure attained after adsorption of H_2 or D_2 by the palladium-carbon. Thus, it follows that complete release of trapped ^4He from the worst case G75-E (A) would result in only 2.2 ppb (parts per billion) of additional ^4He. This is negligible compared with the concentrations of up to 11 ppm found by George[3] and McKubre et al.[4] However, as will be discussed later in this paper, release of trapped atmospheric helium must be considered in this work because of the much lower measured concentrations of ^4He in the H_2 and D_2.

TABLE I

Helium in Palladium-Carbon Specimens

Sample	Mass (mg)	Pd (%)	^4He (Atoms/mg)[a] ($\times 10^9$)	^3He (Atoms/mg)[a] ($\times 10^3$)
G-75E (A)	5.53	0.5	0.73 ± 0.09	3 ± 11
G-75D	5.38	0.4	0.45 ± 0.04	-11 ± 10
G-75E (B)	5.50	0.5	0.24 ± 0.03	-2 ± 8

[a]Uncertainties are estimates of random and systematic errors at a level of 1 sigma.

III.B. Absorption of H_2 and D_2 by Palladium-Carbon and Carbon

When each lead vial was punctured, the pressure was recorded with a small mercury manometer in a known-volume section of the mass spectrometer inlet system. In this way, the amounts of H_2 or D_2 were accurately determined. For pure H_2 or D_2 samples, the measured amounts agreed closely (within 5%) with those calculated from the filling pressure and temperature, and the vial internal volumes. Measurements of the vial internal volumes were made at a later date by sealing the puncture holes with a small blob of epoxy and then re-puncturing the vials in a vacuum system containing a low-sensitivity McLeod gauge. Because of absorption by carbon, the palladium-carbon vials contained much less H_2 or D_2 in the gas phase than originally admitted to the vial. As mentioned previously, the vials on the vacuum manifolds were pinch-sealed as rapidly as possible to minimize contamination by diffusion of atmospheric helium through Pyrex glass sections. During the 10-min sealing time, the H_2 or D_2 pressure was not observed to decrease and, in fact, increased slightly from 152 cm Hg to 153 cm Hg because the pinch-sealing caused a decrease in manifold volume.

Vials containing palladium-carbon analyzed after 5 days in the sandbox at 200°C had only ~23% of the original H_2 or D_2 in the gas phase, with the remainder absorbed in the carbon and not released during the 3-min processing time in the mass spectrometer inlet system. Later tests showed that most (>90%) of the absorbed H_2 or D_2 was released to vacuum in 3 h at 23°C. A summary of the H_2, D_2 results is shown in Fig. 1. It is apparent that in the palladium-carbon vials, there was a rapid decrease in H_2 or D_2 pressure, which reached equilibrium at ~23% of the initial pressure in <5 days, whereas the ordinary activated carbon absorbed H_2 or D_2 at a much slower rate. The carbon data shown in Fig. 1 were fitted to the logarithmic equation $y = -0.16 \ln(x) - 1.2$ which indicates that ~430 days would elapse before the H_2 or D_2 pressure in the carbon-containing vials reached 23% of the initial pressure.

III.C. ^4He Measurements

The ^4He measurements are summarized in Fig. 2 and Table II. The ^4He concentrations in the palladium-carbon

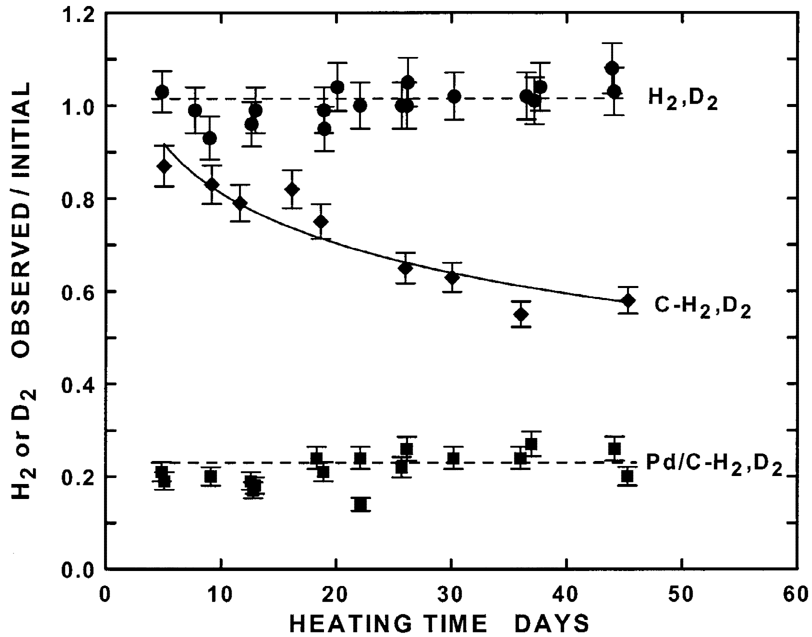

Fig. 1. Ratios of measured H_2 or D_2 amounts in the lead vials to the initial amounts immediately after filling. Horizontal dashed lines were drawn at mean ratios of 1.015 for vials containing only H_2 or D_2 and at 0.23 for vials containing palladium-carbon and H_2 or D_2. The solid line drawn through the carbon points is a least-squares logarithmic fit (see the text).

TABLE II

He-4 Concentrations and R/R_a Values

Sample	N^a	$^4He/(H_2$ or $D_2)$ (ppt)[b]	R/R_a[c]
Pd/C-H_2	9	58 ± 16	0.9 ± 1.0
Pd/C-D_2	8	46 ± 9	2.2 ± 0.7
C-H_2	5	57 ± 20	2.3 ± 1.8
C-D_2	4	42 ± 11	0.5 ± 1.6
H_2	10	62 ± 11	2.0 ± 0.9
D_2	8	54 ± 17	1.7 ± 1.0

[a]N = number of samples analyzed.

[b]Helium concentrations are weighted mean ratios (in parts per 10^{12}) of measured numbers of ^4He atoms to the initial numbers of H_2 or D_2 molecules in the sample vials (see the text). Uncertainties are estimates of random and systematic effects at a level of two standard errors.

[c]$R = {}^3He/{}^4He$ in the sample; $R_a = {}^3He/{}^4He$ in air $= 1.38 \times 10^{-6}$. Values of R/R_a are weighted means and uncertainties are two standard errors.

or carbon vials are expressed relative to the initial H_2 or D_2 immediately after filling and not to the measured H_2 or D_2 when the vials were punctured in the mass spectrometer inlet system. Thus, the ^4He concentrations are expressed relative to the sum of adsorbed and gas phase H_2 or D_2. In the case of palladium-carbon specimens, the concentration excess of ^4He in D_2 versus that in pure D_2 vials is -8 ± 19 ppt (parts in 10^{12}), which indicates an upper limit excess of ~11 ppt at the 95% confidence level. Similar upper limits are obtained when other comparisons are made, for example, palladium-carbon D_2 versus palladium-carbon H_2, although it can be argued that this comparison is not strictly valid because the H_2 and D_2 may have had different initial concentrations of atmospheric ^4He. In this connection, it may be noted that for all three H_2-D_2 comparisons (palladium-carbon, carbon, and H_2 versus D_2), the data show that the removal of traces of atmospheric ^4He was less successful for the H_2 than for the D_2 used to fill the lead vials. The weighted mean ^4He concentration is 60 ± 3 ppt (N = 24) for all H_2 samples analyzed and 45 ± 7 ppt (N = 20) for all D_2 samples.

As mentioned earlier, the amounts of trapped ^4He in the three SRI samples listed in Table I indicate a negligible effect on the ^4He concentrations observed by the SRI researchers[3,4] even if all the trapped ^4He was released during H_2 or D_2 treatment. However, in the work reported here, trapped ^4He in the palladium-carbon is a relatively much larger potential source of ^4He. The palladium-carbon vials contained ~200 mg of the catalyst and were charged with 1.9 cm^3 STP H_2 or D_2 initially. If we take a mean value of 50 ppt for the measured ^4He concentration (see Table II), then it can be calculated that trapped ^4He in the three specimens listed

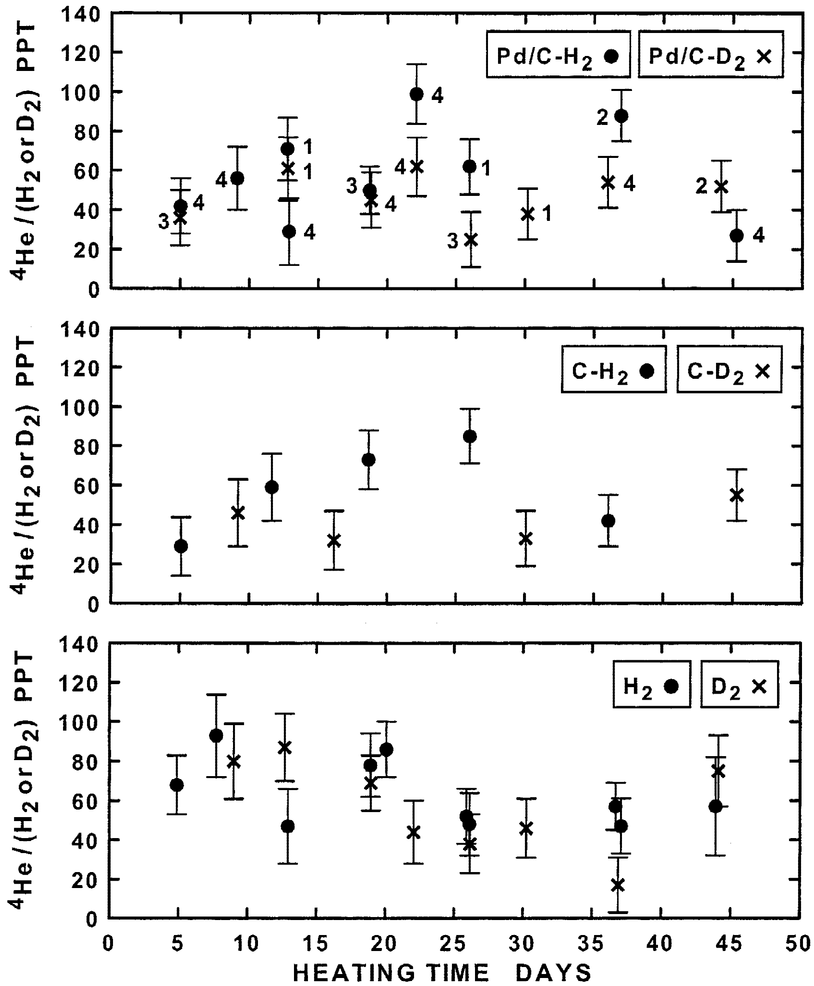

Fig. 2. Concentrations of ^{4}He in H_2 or D_2 in ppt (parts per 10^{12}) versus heating time. The values for palladium-carbon and carbon are expressed relative to the initial amounts of H_2 or D_2 in the lead vials and not to the amounts of H_2 or D_2 in the gas phase at the time of measurement (see the text). Numbers 1, 2, and 3 next to the palladium-carbon points in the top diagram identify the three SRI samples in the order listed in Table I, and the number 4 identifies the sample donated by K. L. Shanahan.

in Table I overshadows measured ^{4}He in the H_2 or D_2 in palladium-carbon vials by factors of 56, 34, and 18. Clearly, practically none of the trapped ^{4}He was released from the palladium-carbon by the action of H_2 or D_2 during the time the vials were in the sandbox at 200°C.

III.D. ^{3}He/^{4}He Ratios

^{3}He/^{4}He ratios given in Table II are expressed relative to the air ratio of 1.38×10^{-6}. Although uncertainties are large because of the very small amounts of ^{3}He in the samples, the results show no evidence for significant nonatmospheric components of ^{3}He or ^{4}He in any of the samples.

IV. SUMMARY

The apparent discrepancy between the ^{4}He results reported in this paper and those given by Case[1,2] is a factor of $\sim 10^7$, if the upper limit concentration excess of $\sim$11 ppt is compared with Case's measured value of 100 ppm. The apparent discrepancy with the SRI results[3,4] is not much better: a factor of $\sim 10^6$. Clearly, something is very different and/or seriously wrong. If Case and the SRI researchers have achieved the "right" conditions in their experiments for ^{4}He to be formed by D-D fusion, then this author must have missed the mark by 6 or 7 orders of magnitude. Because making ^{4}He almost completely vanish inside some sealed metal (lead) vials and/or in the inlet system of the mass spectrometer is not possible, it is reasonable to conclude that observation of significant ^{4}He production depends either on subtle differences in experimental conditions, or on some systematic error that affected the Case and SRI results. On the evidence, this author believes that systematic error is more likely.

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