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

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Measurements of He, ^{3}He/^{4}He, Ne and 13 other components (H_2, HD, D_2, CH_4, H_2O, HDO, D_2O, N_2, CO, C_2H_6, O_2, Ar, and CO_2) in four samples of gas from SRI International (SRI) are reported. Three samples were collected from SRI Case-type stainless steel cells containing ~10 g of Pd/C catalyst initially loaded with ~3 atm D_2 at ~200°C, and the fourth sample (not identified) was stated to be a control. Case and the SRI researchers have claimed to observe ^{4}He in concentrations of ~100 parts per million (ppm) and up to 11 ppm, respectively, produced in these cells via the fusion reaction D + D = ^{4}He + 23.8 MeV. Others found no evidence for ^{4}He addition that cannot be readily explained by leaks from the atmosphere into the SRI cells. One sample appears to be identical in composition to air, and the other three have been seriously affected by leak(s) into and from the SRI cells. The rare gas "forensic" evidence includes ^{3}He/^{4}He ratios and He and Ne concentrations that are almost identical to air values. The samples also show high N_2 (a primary indicator of air), low O_2, and high CO and CO_2 due to reaction of incoming atmospheric O_2 with C in the catalyst. In two samples, the original D_2 (or H_2) has almost completely disappeared by outflow through the leak(s). These results have obvious implications concerning the validity of the excess ^{4}He concentrations claimed by Case and the SRI researchers.

KEYWORDS: *palladium-carbon, helium isotopes, mass spectrometry*

INTRODUCTION

For the sake of brevity, we refer the reader to a recent paper,[1] where the previous works of Case[2,3] and McKubre et al.[4] on production of ^{4}He in Case-type cells are described. In August 1999, McKubre and Tanzella at SRI International (SRI) provided us with three samples of gas from such cells and one sample (not identified) that was stated to be a control.[5] The samples were contained in copper vials ~58 cm^3 in volume, each with a Nupro 4BK valve. The gas pressures in each vial were stated to be ~220, 710, 33, and 900 Torr; the labels indicated that the vials contained deuterium, and a communication from Tanzella[6] also stated that the vials contained deuterium and the ^{4}He concentrations were between 1 and 10 parts per million (ppm). We were informed by the SRI researchers that some of the samples had been collected from Case-type cells that had shown significant excess ^{4}He relative to the dry air value of 5.22 ppm. The SRI researchers have also claimed to observe commensurate excess heat produced by this branch of the D-D fusion reaction. Thus, there was the clear expectation that our analyses would confirm these high ^{4}He concentrations and that the ^{3}He/^{4}He ratios would also reflect production of ^{4}He from D-D fusion.

The vials were initially sent to Pacific Northwest National Laboratory (PNNL), where ^{3}He and ^{4}He analyses were made on small (~6%) aliquots of the gas samples by methods described in Ref. 7. These results were transmitted to SRI in late 1999 (Ref. 8). Then, the vials were sent to McMaster University (McM), where ^{4}He concentrations were determined in small (~2%) aliquots by mass spectrometer peak height comparison with air standards. Measurements of ^{3}He/^{4}He were also made,

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and the vials were leak tested after the remaining gas had been transferred to Corning 1720 glass containers. Subsequently, several aliquots of each sample were transferred to break-seal sample tubes made of Corning 1720 glass. Some of these were sent to PNNL, where measurements of other components were made in a Finnigan MAT 271 mass spectrometer. Other aliquots were reanalyzed recently at McM for ^{3}He/^{4}He ratios and for He and Ne concentrations.

EXPERIMENTAL METHODS AND RESULTS

Leak Tests of the SRI Vials

As mentioned previously, after the initial McM analyses had been made, the remaining gas samples in the SRI vials were transferred to Corning 1720 glass bulbs. The vials were pumped out to high vacuum; then the valves were tightly closed and the vials stored at 24°C for times between 15 and 21 days. Each vial was then attached to the McM mass spectrometer inlet system and the accumulated ^{4}He inside was measured. The results, expressed in time to accumulate 10% of the measured ^{4}He in each vial were ~580, 1020, 480, and 1970 days for vials 46A, 46B, 46C, and 46D, respectively. Thus, we conclude that leaks from the atmosphere into the vials during storage was not a serious source of systematic error in the He, ^{3}He/^{4}He, and Ne measurements.

^{3}He/^{4}He Ratios and Helium and Neon Concentrations

Aliquots varying from 1 to 3% of the gas in each vial were admitted to a vacuum system at McM containing a small mercury manometer and then transferred quantitatively by a mercury Toepler pump to 1720 glass break-seal tubes. The ^{3}He/^{4}He measurements were made at McM in a 10-in.-radius, statically operated mass spectrometer.[9] Helium and neon concentrations were determined in the same instrument by comparison of ^{4}He and ^{20}Ne ion currents from samples with those from accurately known aliquots of air as described previously.[10] A summary of the results is given in Table I. It is apparent that, with the possible exception of 46B, the ^{4}He concentrations are all close to or below the value for dry air of 5.22 ppm. The ^{3}He/^{4}He ratios, expressed relative to air, are practically identical to the atmospheric value of 1.384×10^{-6} (Ref. 9), except for 46C, which shows definite evidence of excess ^{3}He. We believe that this apparent excess ^{3}He was caused by contamination from a vacuum handling system at PNNL. Although this matter is addressed later, at present it may be noted that if 46A, 46B, or 46D had been subject to the same addition of ^{3}He via vacuum line contamination, because of the relatively much larger amounts of He in these three samples, the effects on the ^{3}He/^{4}He ratios would have been negligible. Neon concentrations seem fairly close to the atmospheric value, except for 46C, which shows only 0.6 ppm Ne.

TABLE I

McMaster University Measurements of Helium and Neon*

Sample[a]	^{4}He (ppm)	$\delta_1(^3\text{He})$ (%)[b]	$\delta_2(^3\text{He})$ (%)[c]	Ne (ppm)
46A (2)	5.48 ± 0.19	+0.5 ± 0.4	−0.9 ± 0.4	18.5 ± 0.4
46B (3)	6.52 ± 0.20	+0.2 ± 0.4	−0.4 ± 0.4	20.3 ± 0.4
46C (2)	0.70 ± 0.05	+73.2 ± 2.5	= 0	0.60 ± 0.03
46D (3)	5.30 ± 0.16	+0.4 ± 0.5	−0.1 ± 0.5	18.6 ± 0.04
Air	5.22	= 0		18.2

*Uncertainties are estimates of random and systematic error at a level of one standard deviation.
[a]Numbers in parentheses are numbers of separate aliquots analyzed.
[b]$\delta_1(^3\text{He}) = [\{(^3\text{He}/^4\text{He})_{\text{sample}}/(^3\text{He}/^4\text{He})_{\text{air}}\} - 1] \times 100$.
[c]$\delta_2(^3\text{He})$ values are obtained by subtracting the excess ^{3}He in vial 46C from the ^{3}He amounts found for vials 46A, 46B, and 46D (see the text).

PNNL Finnigan Analyses

Although the initial measurements of He and ^{3}He/^{4}He ratios made at McM in 1999 indicated clearly that air leaking into the SRI Case-type cells was the dominant factor, it was decided to repeat these measurements and also to include Ne assays. Detailed determinations of all other major components were also made at PNNL using a Finnigan MAT 271 mass spectrometer. This instrument is designed for rapid and quantitative analysis of components of gas samples at high sensitivity and high resolution.

The Finnigan mass spectrometer is a 90-deg magnetic sector instrument with a tube radius of 23 cm. Entrance and exit angles of 26.5 deg provide stigmatic focusing, resulting in an effective separation radius of 46 cm. The source magnet strength is 1 T, and the ion source is a thermostatically controlled (±0.1°C) electron-impact design with Einzel lens focusing. Ion accelerating potentials can be varied from 4 to 10 kV, and the effective mass range at 8 kV is 1 to 350 u. Two adjustable-width slits, located between the ion source and the bending magnet, are used to adjust mass resolution ($M/\Delta M$) from 200 to 5000. Ion detection is by electron multiplier or multiple deep-cup Faraday detectors.

Instrument calibration uses high-purity gases to provide mass spectral standards for the permanent gases (N_2, O_2, CO_2, etc.) and low-mass organic compounds. Data-reduction libraries are then constructed, depending on the gas species in the samples, using the pure gas spectrums. Sample and background runs are analyzed using the same methods as the standards. After

background subtraction, the sample spectrum is compared to the specific data-reduction library, and the individual components are deduced by matrix fitting. Partial pressures for each gas component are calculated from the matrix fit, and the ratio of the partial pressures to the total pressure provides the mole percent for each gaseous component in the sample. For the present measurements, the analyses were made at a mass resolution of 200, and the mass scan range was from 2 to 100 u. The sensitivity of the Finnigan system was checked daily using high-purity nitrogen gas. In addition, air standards were run weekly to verify the operation of the instrument.

The results of the Finnigan mass spectrometer analyses are given in Table II. The following features are apparent:

1. All samples show high N_2, which is a primary indicator of air.

2. Sample 46D is most probably room (or outside) air collected by the SRI researchers. Compared to dry air, there is slight addition of H_2O as expected and similar minor additions of other components (H_2, D_2, and CO_2) that are probably due to memory from previous samples in the SRI vacuum system and/or the urban location of SRI.

3. Samples 46A, 46B, and 46C show very low O_2 and very high CO_2 compared to air, and 46A and 46B both show high CO in this sense. These features must be due to significant air leaks in the SRI Case-type cells and chemical combination of incoming atmospheric O_2 with C to form CO and CO_2, facilitated by the Pd/C catalyst inside the cells.

4. Sample 46A is highly deficient in deuterium compared to a presumed initial pressure of ~3 atm, although the observed D/H atom ratio in gaseous hydrogen is 2.2. These facts indicate that the cell originally contained D_2, which was almost completely consumed by three effects: absorption by the Pd/C catalyst,[1] chemical reaction with incoming atmospheric O_2 to form D_2O, and outward loss through the leak(s). Sample 46B is also highly deficient in deuterium, but the D/H atom ratio in gaseous hydrogen is $\lesssim$0.33. These facts indicate that the cell originally contained H_2 (or D_2), which was almost completely consumed by the effects described previously.

5. Sample 46C has the lowest ^4He value of 0.7 ppm, the lowest N_2 value, and the highest H_2 percentage by far. The observed H/D atom ratio in gaseous hydrogen of 16.2 indicates that this cell was initially charged with pure H_2, and that the observed D_2 (and HD) is due to memory in the SRI vacuum system. Although the N_2 value of 1.67%, the O_2/N_2 ratio of 0.10 compared to the value of 0.27 for air, and the high CO_2 value of 2.72% clearly indicate that there was a significant leak in that

TABLE II

PNNL Measurements of Gas Components*

Species	Sample				
	46A	46B	46C	46D	Dry Air
H_2	0.013	0.0064	71.2	0.00063	0.00005
HD	0.025	<0.001	14.7	<0.0004	~0
D_2	0.037	<0.002	0.93	0.041	~0
CH_4	0.0022	0.021	0.81	0.001	0.0002
H_2O	~0.03	~0.20	~0.4	~0.02	0
HDO	~0.01	<0.001	<0.01	~0.001	0
D_2O	~0.01	~0.001	~0.03	<0.0005	0
N_2	86.0	89.1	1.67	78.4	78.1
CO	0.43	0.54	<0.01	<0.001	0.000015
C_2H_6	0.0036	<0.001	0.052	<0.001	~0
O_2	0.58	0.0020	0.16	20.5	20.9
Ar	1.71	1.06	7.28	0.94	0.93
CO_2	11.2	9.10	2.73	0.058	0.035
P_1 (Torr)[a]	220	710	33	900	
P_2 (Torr)[b]	310 ± 9	677 ± 10	45 ± 5	870 ± 12	
V (cm^3 STP)[d]	21.3 ± 0.6	44.0 ± 0.6	3.2 ± 0.3	59.8 ± 0.9	

*All concentration values are in mole percent.

[a]The P_1 values are approximate initial vial pressures provided to us by the SRI researchers.

[b]The P_2 and V values are initial vial pressures (at 25°C) and amounts of gas deduced from manometer measurements made at McM. Uncertainties are estimates at a level of one standard deviation.

cell, it was much less severe than for the other two cells, 46A and 46B.

6. Samples 46A, 46B, and 46C show elevated argon concentrations compared to the air value of 0.93%. For these three samples, excess argon was calculated based on the observed Ar/Ne ratio compared to the value of 504 measured for 46D. The amounts of excess argon in 46A, 46B, and 46C are 0.15, 0.02, and 0.22 cm^3 standard temperature and pressure (STP), respectively. When the vials were received at PNNL, Cajon VCR steel end pieces with copper gaskets were tightly attached to the tube ends beyond the Nupro 4BK valves. Thus, we surmise that argon at ~1 atm pressure was admitted by the SRI researchers to the tube ends of the vials via the leak-testing hole in the end piece before tightening. The fact that 46D does not show excess argon is either due to a slower leak through the Kel-F stem tip of the valve or because less time elapsed between argon filling of the tube end and removal of the end piece immediately before initial helium analyses at PNNL than for the other three vials. In other words, we believe that the high argon values in 46A, 46B, and 46C are artifacts due to reservoirs of argon trapped in the valve end tubes and variable inward leakage of argon through the valve stem tips during storage.

Excess ^{3}He in Sample 46C

Although the $\delta_1(^3\text{He})\%$ value of $+73.2 \pm 2.5$ for 46C indicates a large addition of ^{3}He relative to the atmospheric $^3\text{He}/^4\text{He}$ ratio, the addition is visible only because 46C is the smallest sample and has the lowest ^{4}He concentration. There are two obvious sources for this excess ^{3}He: contamination from the vacuum system at PNNL and decay of contaminant tritium in the D_2 used to fill the relevant cell. These two sources are discussed in turn.

The excess ^{3}He in the vial amounts to 0.6×10^8 atoms. When He isotope dilution measurements were made at PNNL, two aliquots were withdrawn from the vial. It is possible, considering that the ^{3}He blanks and isotope dilution ^{3}He spikes for the vacuum system used are $\sim 10^9$ atoms and $\sim 5 \times 10^{14}$ atoms, respectively, that $\sim 0.3 \times 10^8$ atoms ^{3}He was added to the gas in the vial as each aliquot was taken. If so, then the other vials should be similarly affected. The observed values of $\delta_1(^3\text{He})\%$ for 46A, 46B, and 46D have been corrected on this basis (see Table I). The largest effect is for 46A, where the $\delta_1(^3\text{He})\%$ value changes from $+0.5 \pm 0.4\%$ to $-0.9 \pm 0.4\%$. However, we do not consider that the value of -0.9% should be taken seriously as evidence of addition of ^{4}He from "cold fusion" because $^3\text{He}/^4\text{He}$ variations of up to 4% have been previously noted in laboratory air at McM due to tank helium used in gas chromatographs and the like in nearby laboratories.

In 1989, T/D ratios in commercial D_2O varied from 2.0×10^{-14} to 1.9×10^{-13} (Ref. 11). We estimate T/D ratios from 1.0×10^{-14} to 0.9×10^{-13} for D_2O manufactured in the mid- to late 1990s. These values are applicable to D_2 because all commercial D_2 is made from D_2O. The D_2 will therefore contain more or less radiogenic ^{3}He, labeled as $^3\text{He}_r$, depending on the age of the D_2. If the D_2 gas cylinder used at SRI was 2 yr old, then $^3\text{He}_r/\text{D}$ should be between 1.1×10^{-15} and 1.0×10^{-14}. The measured ratio of excess ^{3}He to D in sample 46C is 7.7×10^{-10}. Thus, it seems that tritium contamination in the D_2 can be ruled out as a source of excess ^{3}He.

SUMMARY

The results of our measurements show that after the Case-type cells at SRI were filled with hydrogen (we will use the term hydrogen to represent D_2 or H_2) at an assumed pressure of ~3 atm and a temperature of ~200°C, the following events probably occurred:

1. The hydrogen pressure in the cell decreased from ~3 to ~0.7 atm during the first few days. Previous work using similar values of pressure, temperature, and hydrogen/catalyst ratio has shown that the Pd/C catalyst absorbs hydrogen surprisingly rapidly to reach an equilibrium pressure in a leak-tight cell at ~23% of the starting pressure within <5 days (Ref. 1). During the early part of this period, the outward flow of hydrogen through leaks in the SRI cells acted to partially prevent the inward flow of atmospheric helium. Several plots of helium concentrations versus time given by McKubre et al.[4] in fact show a near-zero increase of ^{4}He for the first few days of operation of the cells.

2. Incoming atmospheric O_2 started to react with C in the Pd/C catalyst to produce CO and CO_2, although the inflow rate of O_2 was low during the first few days. Nitrogen (N_2) probably behaves like an inert gas and therefore was not absorbed to any great extent by the Pd/C. Remaining hydrogen in the cell leaked outward and also reacted with O_2 (aided by the catalyst) to form D_2O and H_2O. Some of this water was absorbed by the Pd/C, and some escaped outward through the leak(s). During the period from ~5 to 20 days after the start time, atmospheric helium entered the cell (but was not absorbed to any extent by the Pd/C) until the helium partial pressure was close to the atmospheric value of 0.0040 Torr, assuming a total external dry air pressure of 760 Torr. At this stage, the helium partial pressure could not increase any further because the incoming and outgoing helium fluxes were in balance.

We note that two plots of helium concentrations versus time given by McKubre et al.[4] in fact show that the helium concentrations reach maximum values of 9 and 11 ppm at 20 and 27 days, respectively, and then appear to decrease slightly at later times. At the present time, we do not understand why the SRI maximum helium

concentrations are a factor of ~2 higher than the atmospheric value of 5.2 ppm, although the observed increase must surely be due to unrecognized systematic error(s) in the SRI experiments. Although we can think of several reasonable possibilities, these are merely speculative at present, because the experimental details needed to identify the error(s) have not been reported by McKubre et al.[4]

The samples of gas from Case-type cells provided to us by the SRI workers do not show any evidence of production of ^{4}He via cold fusion. Our analytical results can be explained by a combination of two factors: (a) severe leak(s) that allowed air into the cells, and also caused removal of gases including hydrogen from the cells to the atmosphere, and (b) the action of the Pd/C catalyst on O_2 in the incoming air, which resulted in high CO and CO_2 concentrations—telltale fingerprints of chemical combination of atmospheric O_2 and C in the catalyst.

After this technical note was submitted to *Fusion Science and Technology*, we received a communication from McKubre,[12] who stated, inter alia, that sample 46D "was taken directly from a cylinder containing only deuterium gas with approximately 5 ppm helium-4 that we use to calibrate our mass spectrometer." It is therefore very puzzling that this sample, except for slight additions of H_2, D_2, and CO_2, was identical in composition to normal (dry) air. We believe that it is more likely that 46D was room (or outside) air collected by the SRI researchers and that they have overlooked this fact, rather than the remote possibility that the original sample was somehow pumped out and replaced with air during transit from SRI to PNNL, or PNNL to McM. It is worth noting that the helium concentration of 46D was measured to be 5.22 ppm [after taking into account the pressure measured at McM (see Table II)] at PNNL (Ref. 8) soon after arrival from SRI. This value is identical to the known helium concentration in dry air. The helium concentrations for the other three samples measured at PNNL (Ref. 8) by the more precise technique of isotope dilution are in good agreement with the values measured at McM by peak height comparison and listed in Table I. However, apart from these considerations, the fact that "deuterium gas with approximately 5 ppm helium-4" was used to calibrate the SRI mass spectrometer may provide a useful clue as to the cause of the systematic error(s) we believe must have been responsible for the SRI finding of ~11 ppm helium in their Case-type cells. In effect, inward and outward leaks in the SRI Case-type cells (initially charged with pure D_2) ensured that there were large differences in composition between the calibration standards and the actual aliquots of gas removed from the cells for mass spectrometric measurement of ^{4}He at SRI. In our experience, such differences can lead to serious systematic errors. We hope that the SRI researchers will eventually provide sufficient details of their experimental procedures to allow us and other workers to elucidate the nature of these effects.

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