

Preliminary note

Helium production during the electrolysis of D₂O in cold fusion experiments

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INTRODUCTION

Our interest in the "cold fusion" process [1,2] was piqued by the apparent lack of systematic investigation into the composition of the gaseous products produced during the electrolysis of D₂O. A critical issue in determining whether or not the cold fusion process exists is the quality of the evidence concerning the composition of the gaseous products. The low intensity of neutrons has prompted proposals of other fusion processes such as $d + d \rightarrow {}^4\text{He} + \gamma$ [3] and $p + d \rightarrow {}^3\text{He}$ [4,5]. Accordingly, we report the results of experiments designed to detect helium in the effluent gases from electrolysis reactions at palladium cathodes while rigorously excluding possible helium contamination from other sources. The calorimetric electrolysis experiments reported here were performed at China Lake, and the analyses designed to establish the composition of the effluent gases were performed in Austin.

EXPERIMENTAL

The effluent gas from calorimetric electrolytic cells designed to detect excess enthalpy [6,7] was collected with the rigorous exclusion of air, and passed through an activated charcoal cryofiltration system (Fig. 1) to remove all gases except helium [8]. The first stage of the cryofilter acts as a cryopump to sweep any helium entrained in the effluent gas into the filtration system, while the second stage of the cryofilter removes any D₂ that gets past the first stage.

TABLE 1

Reference and detection limit samples

Sample	Contents	Mass spec results ^a	Conclusion
(1)01/08/91	500 ml, vacuum & filled with N ₂ , 3 X	No ⁴ He observed	N ₂ contains no He
(2)01/09/91 A-1	500 ml NWC ^c N ₂ from gas discharge line, cell A	No ⁴ He observed	in spite of accumulation & surge into mass spec.
(3)01/09/91 A-2	500 ml NWC ^c N ₂ from gas discharge line, cell A	No ⁴ He observed	in spite of accumulation & surge into mass spec.
(4) 01/09/91 B-1	500 ml NWC ^c N ₂ from gas discharge line, cell B	⁴ He observed at detection limit ^d	He accumulated then surged into mass spec.
(5) 01/09/91 B-2	500 ml NWC ^c N ₂ from gas discharge line, cell B	No ⁴ He observed	in spite of accumulation surged into mass spec.
(6) 01/16/91 N ₂	500 ml, vacuum & filled with N ₂ , 3 X ; round trip shipment	Large amount of ⁴ He observed ^e	air freight shipment induces flask leakage
(7)01/17/91 N ₂	500 ml, vacuum & filled with N ₂ , 3 X ; round trip shipment	No ⁴ He observed	air freight shipment without leakage
(8) 8x10 ¹¹ ⁴ He atoms	10 mTorr air in 500 ml vacuum	No ⁴ He observed	condensable gas needed to sweep ⁴ He into filter
(9)8x10 ¹¹ ⁴ He atoms	10 mTorr air in 500 ml N ₂	⁴ He observed at detection limit ^d	⁴ He accumulated then surged into mass spec.
(10)1.6x10 ¹¹ ⁴ He atoms	10 mTorr air in 100 ml N ₂	No ⁴ He observed	100 ml flasks not big enough for sampling
(11)8x10 ¹¹ ⁴ He atoms	50 mTorr air in 100 ml N ₂	He observed large peak, long dwell ^e	more ⁴ He observed than expected

^a Mass spectrometer, always at highest sensitivity.^b This result is an example of experiments that were performed routinely to test the N₂.^c NWC = Naval Weapons Center at China Lake, CA.^d Detection limit is approximately 2:1 signal to background ratio, mass spectrometer at highest sensitivity.^e Peak with large signal to background ratio, peak dwelled a long time in mass spectrometer, mass spectrometer at highest sensitivity.

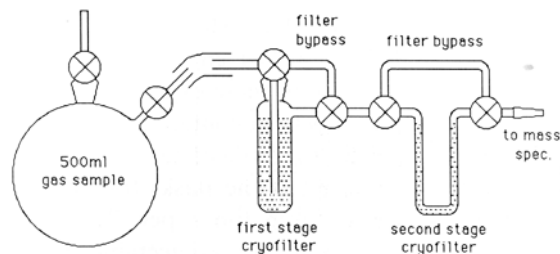


Fig. 1. The two stage activated charcoal cryofilter, designed to remove all gases except helium.

Strenuous efforts were made to avoid contamination of the effluent gas from the electrolytic cell with any external source of helium. A sketch of the cell and gas collection system is shown in Fig. 2. Two identical systems were always run simultaneously using calorimetric cells as described previously [7]. Connections between the cell, flask, and oil bubbler employed thick-walled rubber vacuum tubing. All connecting lines, as well as the cell, were flushed vigorously with boil-off nitrogen, which contained no He (see Table 1), for at least 10 min prior to attaching a gas collection flask. Furthermore, the flasks were generally connected to the cell for at least two days of D₂O electrolysis before removal. The gas evolution rate was calculated to be 6.75 ml min⁻¹ at 528 mA (200 mA/cm²) and 700 Torr assuming ideal gas behavior; thus the 500 ml collection flask was further flushed with more than 19 times its volume of evolving D₂ and O₂ gases per day. Actual measurements of the gas evolution rate by the displacement of water yielded 6.75 ± 0.25 ml min⁻¹ for cell A and 6.69 ± 0.15 ml min⁻¹ for cell B. All solvent additions were made only after vigorously sparging the make-up D₂O with nitrogen for about 5 min. The D₂O was always added through the septum and stopcock into the cell using a gas-tight syringe (Hamilton No. 1005).

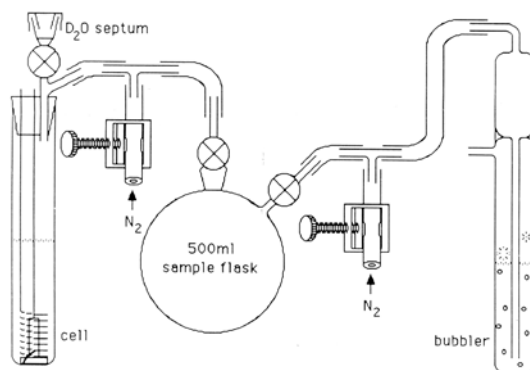


Fig. 2. Electrolytic cell with positive pressure gas discharge line used to collect samples of effluent gas.

Commercially available argon gas, which might be considered as an “inert” atmosphere in these experiments, contained a substantial quantity of He, but nitrogen from liquid N₂ boil-off contained no detectable ⁴He (Table 1). The palladium rod cathodes (Johnson Matthey, 99.96%, $A = 2.64 \text{ cm}^2$, $K = 0.35 \text{ cm}^3$) were wet polished with silicon carbide paper prior to use in these experiments. This surface treatment would likely remove any measurable helium contamination in the palladium [9]. Collection flasks were prepared in Austin for effluent gas collection at China Lake by applying a 10 mTorr vacuum (measured at the flask) followed by filling with boil-off N₂. This process was repeated three times per flask. The collection flasks (500 ml) processed by this method contained no detectable ⁴He.

Mass spectral measurements were made using a Bell & Howell 21-491 mass spectrometer. The mass spectrometer had sufficient resolution to separate D₂ and He easily when the mass peaks were displayed as analogue signals on an oscilloscope. After removing the air from the cryofilter by evacuating and flushing the filters with nitrogen multiple times, the evacuated filters were connected to the mass spectrometer, and the gas

collection flask was attached to the filters using a short section of thick-walled rubber tubing; then the air in the rubber tubing was evacuated through the two filter bypasses as shown in Fig. 1. The filters were then cooled by immersion in liquid nitrogen for several minutes whereupon the stopcocks were manipulated to open the collection flask to the first stage of the cryofilter for approximately 10 s while the stopcock to the second stage remained closed. After allowing at least 1 min for adsorption of the effluent gas into the activated charcoal of the first stage cryofilter, the stopcock to the second stage cryofilter was opened. Concurrently, the valve controlling the evacuation of the ion source of the mass spectrometer was closed to enhance sensitivity by preventing rapid evacuation of the sample from the source. If helium had not been observed after approximately 3 min, then the inlet to the ion source of the mass spectrometer was valved off, and any helium diffusing through the cryofilter was allowed to accumulate between the filter and the valve. The opening of this inlet to the mass spectrometer surged any helium present into the source, thus enhancing the concentration of the helium to be observed. When operated in this manner, there is enough effluent gas in one 500 ml flask to perform two helium determinations should the results of the first determination be ambiguous for any reason. As demonstrated by samples 6-9 in Table 1, the detection limit for helium is approximately 8×10^{11} atoms of ^4He in the gas condensed into the cryofilter.

RESULTS

The reproducibility of our method for collecting gaseous samples and analyzing for helium is illustrated by the data presented in Table 1. No helium was detectable in routinely repeated experiments involving collection flasks filled with boil-off nitrogen (Sample 1). Collection flasks (500 ml) were then filled with boil-off nitrogen at Austin and shipped to China Lake where they were either connected to the gas collection system and flushed with boil-off nitrogen (Samples 2-5) or simply returned unopened (Samples 6,7). These flasks contained no detectable ^4He except in two cases (Table 1). We ascribe the miniscule amount of ^4He detected in Sample 4 (01/09/91 B-1) and the large amount of He detected in Sample 6 (01/16/91 N_2) to air leaks that may have occurred during shipment by air freight due to reduced atmospheric pressure in flight. Deuterium oxygen mixtures could not be shipped by air freight due to the explosion hazard. Thus the nitrogen standard Samples 2-7 in Table 1 represent worst case situations.

TABLE 2

$\text{D}_2\text{O} + \text{LiOD}$ electrolysis. The presence of helium in the effluent gas compared to the generation of excess power and heat

Sample	P_{ex}/W	$\Delta H_{\text{out}}/\Delta H_{\text{in}}$	Results ^a
(1) 12/14/90 A	0.52 ^b	1.20/1 ^b	^4He observed as large peak, long dwell; no ^3He ^b
(2) 05/05/75 B	0.46	1.27/1	^4He observed as large peak, long dwell ^c
(3) 11/25/90 B	0.36	1.15/1	^4He observed as large peak, long dwell; no ^3He ^b
(4) 11/14/79 B	0.17	1.12/1	^4He observed at detection limit; no He
(5) 04/29/65 A	0.24	1.10/1	^4He observed medium peak, some dwell; no ^3He
(6) 11/27/90 A	0.22	1.09/1	^4He observed as large peak, long dwell ^c
(7) 03/26/69 A	0.14	1.08/1	^4He observed at detection limit; no He
(8) 01/18/37 A	0.07	1.03/1	No ^4He or ^3He observed
(9) 12/17/906	0.29 ^d	1.11/1 ^d	No ^4He or ^3He observed ^d

^a Mass spectrometer, always at highest sensitivity.

^b Current was 660 mA, all other experiments used 528 mA.

^c No measurement of ^3He was made.

^d The D_2O solution level of the cell was found to be excessively low resulting in an erroneous calorimetric result.

The ^4He detection limits (Samples 8-11 in Table 1), the purity of the flush gas (Samples 1-7), and our ability to exclude He contamination from the air were determined concurrently with the analyses of effluent gas samples from China Lake. We believe that the analysis of effluent gas produced by the electrolytic cells are definitive. The results tabulated in Table 2 indicate that the effluent gases contained He when electrolysis of D_2O produced significant excess heat and power. A second measurement was performed when the first measurement was ambiguous. The helium detection limit of our technique is approximately 0.14 W in terms of excess power (P_{ex}) or about 1.08/1 in heat ratios ($A_{\text{out}}/A_{\text{in}}$), with the calorimetry being accurate to 3% ($\pm 0.03/1$). The excess power of 0.14 W (8% excess heat) reported in Table 2 corresponds to approximately 2×10^{12} atoms of ^4He

in a 500 ml flask as referenced to the 10 mTorr air in 500 ml of N₂ (Table 1). The excess power observed is roughly proportional to the concentration of helium in the effluent gas within the limits of experimental resolution. The calorimetric results reported in Table 2 were measured shortly before the removal of the gas collection flask; however, fairly constant values were obtained throughout the day.

In a preliminary experiment, dental X-ray films were positioned near the outer surfaces of two operating D₂ + LiOD electrolytic cells in an attempt to detect ionizing radiation. In both instances, the dental films were found to be significantly exposed when developed. It was not possible for hydrogen or deuterium to sensitize the film because the cells were completely sealed for effluent gas analysis. A cell containing H₂O + LiOH and producing no excess heat gave no exposure of the film in a similar experiment.

TABLE 3
H₂O + LiOH electrolysis. Checking for ⁴He in effluent gas

Sample	Results
(1) 1/9/91 A-2	No ⁴ He or ³ He observed
(2) 1/16/91 A	No ⁴ He or ³ He observed
(3) 1/16/91 AA	No ⁴ He or ³ He observed
(4) 1/16/91 B	No ⁴ He or ³ He observed
(5) 1/17/91 A	No ⁴ He or ³ He observed
(6) 1/17/91 B	No ⁴ He or ³ He observed

Mass spectrometer, always at highest sensitivity; any gas passing through the cryofilter was allowed time to accumulate and then surged into the mass spectrometer.

As a final experiment, the D₂O + LiOD in the electrolytic cells was replaced by H₂O + LiOH to serve as a control experiment. The H₂O + LiOH electrolysis, being conducted in an identical manner to the D₂O + LiOD electrolysis, is the best indication of our ability to exclude ⁴He contamination from the air. However, fusion via the p + d → ³He pathway cannot be ruled out either theoretically [4,5] or experimentally [10] since our palladium electrodes likely retained some deuterium from the previous experiments. Although some unexplained excess heat effects were observed, no ³He or He was detected (Table 3). Furthermore, no exposure of dental X-ray films occurred in these H₂O + LiOH/Pd cells.

DISCUSSION

The use of the activated charcoal cryofilter removes the interfering D₂ and O₂ from the effluent gas allowing unambiguous observation of helium by mass spectrometry. Further, He can be identified in the presence of D₂ because of its higher ionization potential; likewise He can be distinguished from HD. As the accelerating voltage of the electron gun ionizer in the mass spectrometer is lowered, helium related peaks will disappear due to a decrease in ions produced, but molecules incorporating isotopes of hydrogen will continue to be ionized.

All of the relevant analyses were performed with the mass spectrometer at its highest sensitivity setting. Strenuous efforts to prevent helium infiltration due to air leaks were generally successful. Had gross air leaks occurred, helium would have been detected at concentrations several orders of magnitude above those observed.

The concentration of helium (⁴He) observed in the gaseous products maintained an approximate correspondence to the amount of excess power measured in the electrochemical calorimetric cells (Table 2). This indicates that He is produced at or near the surface of the palladium electrode rather than deeper in the bulk metal and that the preponderance of the helium escapes from the electrode and resides in the effluent gas. Another study of helium in electrolyzed palladium tends to support this behavior [9].

Although the exact nature of the fusion reaction or reactions producing the excess heat effect is not known, the process



can be used as a basis for an estimate of helium production. For this fusion process, 1 W corresponds to the production of 2.66×10^{11} He s⁻¹. The highest excess power observed at 528 mA (0.46 W or 1.3 W/cm³, Sample 2 in Table 2) would therefore produce 5.4×10^{14} atoms of He in the time period required to fill the 500 ml collection flask with D₂ and O₂ gases (4440 s). It is apparent from Table 1 that this amount of He would be more than two orders of magnitude above the detection limit for the analytical method used in this

study. The large amount of He observed in this experiment (Table 2) is likely to be within an order of magnitude of this theoretical estimate of helium production.

CONCLUSIONS

Our cold fusion experiments show a correlation between the generation of excess heat and power and the production of He, established in the absence of outside contamination. This correlation in the palladium/D₂O system provides strong evidence that nuclear processes are occurring in these electrolytic experiments. The major gaseous fusion product in D₂O + LiOD is ⁴He rather than ³He. No helium products are found in H₂O + LiOH experiments. These results add to the accumulating evidence for cold fusion that involves 12 countries and more than 70 laboratories [11].

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