HEAT AND HELIUM PRODUCTION IN COLD FUSION EXPERIMENTS

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ABSTRACT

A critical issue in determining whether or not the cold fusion process exists is the measurement of nuclear products in amounts sufficient to match the excess heat effects. Calorimetric evidence of excess heat up to 27% was measured during the electrolysis of heavy water using palladium cathodes. Effluent gas samples collected during episodes of excess heat production and sent to the University of Texas for analysis by mass spectrometry showed the presence of $^4$He. Furthermore, the amount of helium detected correlated approximately with the amount of excess heat and was within an order of magnitude of the theoretical estimate of helium production based upon fusion of deuterium to form $^4$He. Control experiments performed exactly the same but using H$_2$O + LiOH in place of D$_2$O + LiOD gave no evidence for helium.

INTRODUCTION

It is now known that the observation of cold fusion effects in electrochemical cells [1, 2] requires special attention to many details such as cell geometry, electrode arrangements, current density, deuterium loading, and control of impurities as well as considerable patience [3]. Our initial efforts, representing five months of research, did not produce any measurable excess heat effects [4]. In retrospect, it is not surprising that many research groups were unsuccessful in their few weeks of frenetic cold fusion activities [5]. The low intensity of neutrons has prompted proposals of cold fusion processes that yield only heat and helium as products [6-9]. We report here the results of electrochemical calorimetric experiments designed to detect helium in the effluent gases while rigorously excluding possible helium contamination from other sources.
EXPERIMENTAL

The electrolysis cell initially contained 18 g of 0.2 M LiOD + D₂O (99.9%, Cambridge Isotope Laboratories). The palladium rod cathode (Johnson Matthey, 99.96%, d = 0.63 cm, l = 1.1 cm) was spot-welded to a nickel lead. A tightly-wound coil of Pt-20% Rh (5.35 g, d = 0.1 cm) served as the counter electrode and was symmetrically positioned about 0.3 cm from the cathode. Both the anode and cathode leads were covered with heat shrinkable Teflon tubing to prevent exposure of the bare metal to the gases in the headspace. Two identical isoperibolic calorimetric cells were always run in series (cells A and B) in a constant temperature bath set at 27.50 °C. Details of the calorimetric cell design and determinations of the calorimetric constants (Kᵢ) are given elsewhere [10]. Previously determined mean values of these constants [10] were used in this study (K₁ = 0.138 W/°C, K₂ = 0.143 W/°C and K₄ = K₅ = 0.135 W/°C for the two thermistors in each cell). The constants were determined in four separate experiments over a one-year period and showed no significant change with time.

Strenuous efforts were made to avoid contamination of the effluent gas from atmospheric helium. The system was always under positive pressure since the effluent gas was evolved through an oil bubbler. Details of the gas collection system are given elsewhere [11]. The entire system was thoroughly flushed with boil-off nitrogen that contained no detectable helium [11]. Furthermore, the system was self-flushing due to the steady evolution of D₂ and O₂ gases. The gas evolution rate was calculated to be 6.73 mL min⁻¹ at 528 mA (200mA/cm²) at 297 K and 700 Torr assuming ideal gas behavior. 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. This data adds to the substantial evidence that excess enthalpy effects are not explainable by the recombination of D₂ and O₂ gases within the cell [10, 12].

The effluent gas samples collected at the Naval Weapons Center in 500 mL flasks were sent to the University of Texas for analysis by mass spectrometry. A cryofiltration system was employed to remove all gases except helium [11]. Nevertheless, mass spectral measurements had sufficient resolution to baseline separate D₂ and ⁴He. Based on air samples collected in the Chemistry Laboratory at the University of Texas and assuming a normal helium concentration of 5.22 ppm by volume [13], the detection limit for helium in our measurements is approximately 8 x 10¹¹ atoms of ⁴He in 500 mL of gas sample [11].
RESULTS

A portion of the calorimetric studies using palladium rod cathodes in 0.2 M LiOD + D$_2$O are presented in Fig. 1. The equation

$$X = \frac{\text{Heat out}}{\text{Joule heat in}} = \frac{K \Delta T}{(E - E_0^0) I}$$

(1)

was used where $K$ is the calorimetric cell constant, $E$ is the cell voltage, $E_0^0$ is the thermal neutral potential, and $\Delta T$ is the temperature difference [10]. Excess enthalpy is present when $X>1.00$ where $X$ is the daily mean value of the heat ratio. Gas sample collection dates for helium analysis are given for cells A and B, thus the highest excess enthalpy (27%) was observed on 10/21/90 in cell B. This value may actually be somewhat higher since the week-end room temperature (21.5°C) was cooler than normal. The first 12 days are not shown in Fig. 1 due to several shut-downs of the electrolysis to correct leaks in the gas collection system. No significant excess enthalpy effects were observed in the first 10 days. These calorimetric measurements continued until the two cells were turned off on December 25. Calorimetric results around the 12/17/90 time period are questionable due to unusual increases in cell voltages with time as the D$_2$O solution level dropped below the electrode level.

Fig. 1. Sample of calorimetric measurements and effluent gas collection dates in D$_2$O + LiOD.
The helium analysis results in Table 1 show that the effluent gases contained $^4\text{He}$ when the electrolysis of $\text{D}_2\text{O}$ produced significant excess heat and power. No $^3\text{He}$ was detected [11]. Small peaks near the detection limit of the mass spectrometer are assigned a value of $10^{12}$ atoms of $^4\text{He}$ per 500 mL of effluent gases. Medium peaks were roughly an order of magnitude greater while large peaks were about two orders of magnitude above the detection limit. The values reported for the excess power ($P_{\text{EX}}$) and heat ($X>1.00$) are those measured within 1-2 hours of removing the gas collection flask in order to obtain the best time correlation. The excess heat and power measurements were always quite steady during this time period. The samples are arranged in order of decreasing power except for the 12/17/90 samples where the low $\text{D}_2\text{O}$ levels likely created calorimetric errors. Nevertheless, these samples also show more helium in the cell that produced more excess heat. The only sample not listed in Table 1 is 12/14/90-B that broke during shipment. The input power for each measurement is given by $P_{\text{EX}}/X-1.00$, hence the input power is 2.60 W for the 12/14/90-A sample.

Results of dental film experiments are shown in Fig. 2. The film that was wrapped around the outside of the electrolysis cell A and hence closest to the palladium showed the greatest exposure. Clear regions are due to a peeling away of the emulsion rather than non-exposure. The film in cell B was further away from the palladium and deeper in the secondary compartment, hence the bottom half was somewhat shielded by the Teflon pedestal used to hold the palladium in position [10]. This film showed partial exposure for the top portion and less exposure near the bottom portion where any direct radiation would

<table>
<thead>
<tr>
<th>Sample</th>
<th>$P_{\text{EX}}$ (W)</th>
<th>$X$</th>
<th>$^4\text{He}$ Atoms/500 mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>12/14/90-A</td>
<td>0.52$^a$</td>
<td>1.20$^a$</td>
<td>$10^{14}$ (large peak)</td>
</tr>
<tr>
<td>10/21/90-B</td>
<td>0.46</td>
<td>1.27</td>
<td>$10^{14}$ (large peak)</td>
</tr>
<tr>
<td>11/25/90-B</td>
<td>0.36</td>
<td>1.15</td>
<td>$10^{14}$ (large peak)</td>
</tr>
<tr>
<td>11/20/90-A</td>
<td>0.24</td>
<td>1.10</td>
<td>$10^{13}$ (medium peak)</td>
</tr>
<tr>
<td>11/27/90-A</td>
<td>0.22</td>
<td>1.09</td>
<td>$10^{14}$ (large peak)</td>
</tr>
<tr>
<td>10/30/90-B</td>
<td>0.17</td>
<td>1.12</td>
<td>$10^{12}$ (small peak)</td>
</tr>
<tr>
<td>10/30/90-A</td>
<td>0.14</td>
<td>1.08</td>
<td>$10^{12}$ (small peak)</td>
</tr>
<tr>
<td>10/17/90-A</td>
<td>0.07</td>
<td>1.03</td>
<td>$&lt;10^{12}$ (no peak)</td>
</tr>
<tr>
<td>12/17/90-A</td>
<td>0.40$^b$</td>
<td>1.19$^b$</td>
<td>$10^{13}$ (medium peak)</td>
</tr>
<tr>
<td>12/17/90-B</td>
<td>0.29$^b$</td>
<td>1.11$^b$</td>
<td>$&lt;10^{12}$ (no peak)</td>
</tr>
</tbody>
</table>

$a$ i = 250 mA/cm². All other experiments used i = 200 mA/cm².

$b$ Possible calorimetric errors due to low $\text{D}_2\text{O}$ solution levels. No $^3\text{H}$ was detected. Mass spectrometer always at highest sensitivity.
have to pass through the Teflon pedestal. These films were in distilled water contained in the secondary (gap) compartment [10]. The control film was immersed in distilled water for the same time period and showed only scattered exposure due to background radiation. Samples of fresh films with no exposure and total exposure are also shown for comparisons. Cell A was producing the larger excess heat effect when the film was first inserted, but cell B produced the larger effect in the seven days that followed.

![CELL A](image1)

![CELL B](image2)

![CONTROL](image3)

![NO EXPOSURE](image4)

![70 KV, 7 mA, 0.5 SEC](image5)

**Fig. 2.** Results of dental film experiments.

In a following control experiment of major importance in proving helium production, \( \text{H}_2\text{O} + \text{LiOH} \) was used in place of \( \text{D}_2\text{O} + \text{LiOD} \), yet the same cells, electrodes, gas lines, and collection flasks were employed exactly as with \( \text{D}_2\text{O} \). Results of the \( \text{H}_2\text{O} \)-control experiments are shown in Table 2. No helium was observed in any experiment. The \( \text{H}_2\text{O} + \text{LiOH} \) electrolysis, conducted in an identical manner to the \( \text{D}_2\text{O} + \text{LiOD} \) electrolysis, is the best indication of our ability to exclude \( ^4\text{He} \) contamination from the air. The \( \text{H}_2\text{O} + \text{LiOH} \) experiments did not produce any significant excess heat or exposure of dental film. The mean calorimetric values for 15 days of electrolysis are \( \overline{X}_1 = 1.025 \pm 0.02, \overline{X}_2 = 1.035 \pm 0.03 \) for cell A and \( \overline{X}_4 = 1.01 \pm 0.02, \overline{X}_5 = 1.00 \pm 0.03 \) for cell B at the 99% confidence interval (\( \pm 2.58 \sigma/\sqrt{n}, n = 15 \)). Earlier reports of unexplained excess heat effects in \( \text{H}_2\text{O} + \text{LiOH} \) [11] were due to the dental film studies. The secondary compartments containing the films were not tightly sealed, hence loss of water by evaporation or possibly by a wicking action created a calorimetric error. We reported previously that there is a 2% increase in \( X \) per mL of \( \text{H}_2\text{O} \) lost from the gap [10].
Table 2. Results of H$_2$O + LiOH Control Experiments.

<table>
<thead>
<tr>
<th>Sample$^a$</th>
<th>Results$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/16/91-A</td>
<td>No $^4$He or $^3$He observed</td>
</tr>
<tr>
<td>1/16/91-AA</td>
<td>No $^4$He or $^3$He observed</td>
</tr>
<tr>
<td>1/16/91-B</td>
<td>No $^4$He or $^3$He observed</td>
</tr>
<tr>
<td>1/17/91-A</td>
<td>No $^4$He or $^3$He observed</td>
</tr>
<tr>
<td>1/17/91-B</td>
<td>No $^4$He or $^3$He observed</td>
</tr>
</tbody>
</table>

$^a$ Used same cells, electrodes, gas lines, and collection flasks as in D$_2$O experiments. $i = 200$ mA/cm$^2$.

$^b$ Mass spectrometer always at highest sensitivity. Any gas passing through the cryofilter was allowed time to accumulate and then surged into the mass spectrometer.

Previous calculations suggest that neutron activation of indium or gold foils should occur for flux levels of $10^4$ s$^{-1}$ if the foils are placed at the outer glass surface of our electrochemical cell [14]. No activation of indium or gold foils was detected in this study, hence the average neutron flux was less than $10^5$ s$^{-1}$ during the time period that these foils were in the cells. The detection of neutron flux levels as low as $10^3$ s$^{-1}$ is possible for gold foils, however the foils used in our experiments were lost for about a week despite express shipment to E. G. and G. Rocky Flats Inc., Golden, Colorado, for activation analysis.

**DISCUSSION**

The amount of helium ($^4$He) observed in the gaseous products maintained an approximate correspondence to the amount of excess power or heat observed in electrochemical calorimetric cells (Table 1). This indicates that $^4$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. Several theories have predicted this behavior [9, 15].

Although the exact nature of the fusion reaction(s) producing the excess heat effect is not known, the process

$$^2$$D + $^2$D $\rightarrow$ $^4$He + 23.8 MeV (lattice) \hspace{2cm} (2)$$

can be used as a basis for an estimate of helium production. For this fusion process, 1 W corresponds to a rate of $2.62 \times 10^{11}$ $^4$He s$^{-1}$. The highest excess power observed at 528 mA (0.46 W, 10/21/90-B, Table 1) would therefore produce $5.4 \times 10^{14}$ atoms of $^4$He in the time period required to fill the 500 mL collection flask with D$_2$ and O$_2$ gases (4440 s).
About $10^{14}$ atoms of $^4$He were detected which is within experimental error of the theoretical amount.

Despite the approximate correlation of excess heat and helium, possible error sources proposed by cold fusion critics include air contamination, helium diffusion into the glass flask, and the escape of helium contained in the palladium rod. Ignoring the helium/heat relationship (Table 1), the simple yes or no detection of helium in 7/7 experiments producing excess heat and the absence of helium in 6/6 experiments not producing excess heat (1 in D$_2$O, 5 in H$_2$O) implies a chance probability of $(1/2)^{13} = 1/8192$ or 0.0122%.

The diffusion of helium through glass is a valid concern and can be expressed by

$$q = \frac{KP}{d} \quad (3)$$

where $q$ is the diffusion rate, $K$ is the permeability, $P$ is the partial pressure of helium, and $d$ is the glass thickness [16]. The value of $K$ varies greatly with the type of glass, its treatment, and temperature [16]. For the Pyrex glass flasks used in this study, theoretical calculations yield $q = 1.5 \times 10^{10}$ He cm$^{-2}$ day$^{-1}$ or $4.7 \times 10^{12}$ He day$^{-1}$ ($A = 314$ cm$^2$). Experimentally, however, there is no measurable evidence for any effect due to helium diffusion through glass. The amount of helium observed versus the time interval that the effluent gas sample resided in the glass is shown in Fig. 3. For D$_2$O-LiOD experiments, high and low helium levels occur at both short and long time intervals that ranged from 14 to 61 days. In fact, the least square line shows a negative correlation if any exists at all. For H$_2$O-LiOH experiments, no helium was detected for gas resident periods up to 20 days. The N$_2$-filled flasks were often shipped by air and had shorter time intervals for helium diffusion.

A possible explanation for the lack of measurable helium diffusing through the glass is the opposing flow of deuterium or hydrogen out of the glass. Since D$_2$ makes up 2/3 of the gas within the flask, its rate of diffusion outward is about 3 orders of magnitude greater than the diffusion of atmosphere helium into the flask. Helium and hydrogen (deuterium) diffuse through glass by similar mechanisms and sites [16] and show similar kinetic parameters [17]. Furthermore, hydrogen removes helium from glass [18]. Although no specific literature study could be located that investigated the effect of hydrogen on the diffusion of helium through glass, Paneth and Peters [19] reported that after 15 days less than $3 \times 10^9$ He atoms had diffused into a 3 liter flask ($A = 1300$ cm$^2$) containing 10 Torr of hydrogen gas.
Samples of our unused palladium were analyzed for helium by Rockwell International. No $^3\text{He}$ or $^4\text{He}$ was observed in any of our palladium samples. In terms of helium concentrations, the uncertainties correspond to less than $10^8$ atoms/mg for $^3\text{He}$ and $^4\text{He}$. This indicates that our palladium cathodes originally contained less than $5 \times 10^{11}$ He atoms, hence any helium originally present in the palladium electrode is not sufficient to explain our helium measurements. Furthermore, the same palladium electrodes were used in prior experiments [10]. A sample of the palladium electrode used in these $\text{D}_2\text{O} + \text{LiOD}$ and $\text{H}_2\text{O} + \text{LiOH}$ experiments also failed to show any significant level of $^3\text{He}$ or $^4\text{He}$. This result, however, is somewhat inconclusive since the palladium electrodes were polished after the $\text{D}_2\text{O}$ study that produced excess heat and helium and then were used in the $\text{H}_2\text{O} + \text{LiOH}$ study (Table 2).

The reproducibility of our excess heat and helium results was recently demonstrated by using a modification of the Szpak co-deposition method [20]. Palladium and deuterium were simultaneously deposited onto our Pd rods using 0.3 M LiCl to produce the excess enthalpy effect. Effluent gas samples sent to a commercial laboratory yielded $7.0 \pm 2$ ppb $^4\text{He}$ or $8.5 \times 10^{13} \text{He}/500 \text{ mL}$ for a cell producing 0.14 W of excess power ($X = 1.12$) at 528 mA. This sample was within a factor of two of the theoretical $^4\text{He}$ based on Eqn. 2.
A second gas sample gave 7.5 ± 2 ppb $^4$He or $9.2 \times 10^{13}$ $^4$He/500 mL for a cell producing 0.54 W of excess power ($X = 1.25$) at 874 mA. Some recombination of D$_2$ and O$_2$ was observed in this cell, hence the measured excess heat and power is too high. Nevertheless, the amount of $^4$He was within a factor of four of the theoretical. It should be stressed that these recent experiments involved a different electrolysis method, employed a different person collecting the gas samples, and had a different laboratory doing the helium analysis, yet the results gave $^4$He amounts even closer to the theoretical.

The major errors in our calorimetric measurements are likely fluctuations in the room temperature and fluctuations in the cell voltage due to gas bubble effects. These error sources limit our accuracy to about ±0.04 W or about ±2%. Nevertheless, the major error source in correlating the amount of helium with the excess enthalpy is in the helium analysis. Improved measurements of helium and excess enthalpy could precisely identify the energy of the dominant fusion reaction. Experiments to do this are in progress.

CONCLUSIONS

Our cold fusion experiments show a direct correlation between the time of generation of excess heat and power and the production of $^4$He, established in the absence of outside contamination. This correlation in the palladium/D$_2$O system provides strong evidence that nuclear processes are occurring in these electrolytic experiments and that helium is produced at or near the surface of the palladium rather than deeper in the bulk metal. The major gaseous fusion product in D$_2$O + LiOD is $^4$He rather than $^3$He. No helium products are found in H$_2$O + LiOH experiments.

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