This file includes five papers that relate to a dispute between Jones et al. and Miles.

Jones, S.E. and L.D. Hansen, *Examination of claims of Miles et al in Pons-Fleischmann-Type cold fusion experiments*. J. Phys. Chem., 1995. **99**: p. 6966.

Miles, M., *Reply to 'Examination of claims of Miles et al. in Pons-Fleischmann-type cold fusion experiments'*. J. Phys. Chem. B, 1998. **102**: p. 3642.

Jones, S.E., L.D. Hansen, and D.S. Shelton, *An assessment of claims of excess heat in cold fusion calorimetry*. J. Phys. Chem. B, 1998. **102**: p. 3647.

Miles, M., *Reply to 'An assessment of claims of excess heat in cold fusion calorimetry'*. J. Phys. Chem. B, 1998. **102**: p. 3648.

Shelton, D.S., et al., *An assessment of claims of 'excess heat' in 'cold fusion' calorimetry*. Thermochim. Acta, 1997. **297**: p. 7.

Examination of Claims of Miles et al. in Pons–Fleischmann-Type Cold Fusion Experiments

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In cold fusion experiments conducted at the Naval Research Laboratory in China Lake, M. H. Miles and co-workers claim to have produced excess heat correlated with helium-4 production, X-rays, and Geiger-counter excitation. However, scrutiny of the claims shows that unreliable calorimetric and nuclear-product detection methods were used. Moreover, inconsistencies and errors are found in the data and data analysis. The juxtaposition of several poor techniques and inconsistent data does not make a compelling case for cold fusion. We conclude that the evidence for cold fusion from these efforts is far from compelling.

Introduction

This paper scrutinizes claims of excess heat, X-rays, Geiger-counter excitation, and helium-4 production in cold fusion experiments by M. H. Miles and co-workers.[1–8] It is specifically written in response to a request from M. H. Miles:[9]

> I hereby challenge Professor Jones to take his allegations regarding my work to a refereed scientific journal... I hope this matter can thus be resolved without any further actions.

Miles et al. claim:[2]

> Our electrochemical experiments unambiguously show a direct correlation between the time of generation of excess enthalpy and power and the production of ^{4}He... This correlation in the palladium/D_2O system provides strong evidence that nuclear processes are occurring in these electrolytic experiments and that helium is produced... In summary, nuclear events with ^{4}He as a major product occur during the electrolysis of the Pd/D_2O + LiOD system.

These bold claims warrant scrutiny, especially since these are the *only* published claims for concomitant excess power, helium-4, and X-ray production. Careful examination of the papers shows that unreliable calorimetric and analytical methods were used, incorrect statistical procedures were applied, and there are inconsistencies in the results. Thus, we find these experiments to be ambiguous and the claims of "excess heat" and excess heat/nuclear product correlations to be invalid.

Claims of Helium-4 Production in Electrolytic Cells

Figure 1 displays data tables published in 1991[3] and 1993.[6] Published plots of helium-4 data are shown in Figure 2. Inspection of the tables in Figure 1 shows that the same data are involved. Note that values of ^{4}He atoms/500 mL fall at 10^{12}, 10^{13}, and 10^{14} in Table 1. The lack of values between integer exponents implies a crude estimation procedure. Indeed, the authors state[3] (emphasis added by Jones and Hansen):

> *Small* peaks near the detection limit of the mass spectrometer are *assigned* a value of 10^{12} atoms of ^{4}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.

A striking change occurs in the same data presented in 1993; the values of ^{4}He atoms/500 mL are *10-fold* greater and now in putative agreement as to the order of magnitude of the ^{4}He rate required to account for the claimed excess heat rate, i.e., about 5×10^{14} atoms/4440 s.[2] Such an amplification diminishes confidence in the claims. Note also the changes in footnoting which lead to an uncertainty in which runs had a current density of 250 mA/cm^2 instead of 200 mA/cm^2 and which are subject to calorimetric error.

Comparison of parts A and B of Figure 2 also shows differences in presentation of the same data. In ref 3 (Figure 2A), five points are displayed at the "large peak" value whereas in ref 6 (Figure 2B), only four are shown. In ref 6, two values are plotted each at "medium", "small", and "no peak" positions, whereas in ref 3, there is only one point at the "medium" and four points at the "no peak" position. The plot in ref 3 does not agree with the table from ref 3.

An additional data point showing some He in a N_2-filled control flask appears in the plot from ref 6. Neither plot shows all of the data points from ref 4, which discloses significant amounts of He in N_2-filled flasks. Two of ten of these control flasks gave "large" amounts of ^{4}He and two gave "small" amounts.

In evaluating the statistical significance of their results, the authors stated in 1991:[3]

> 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_2O, 5 in H_2O) implies a chance probability of only $(1/2)^{13} = 1/8192$ or 0.0122%.

Using the same data set, the authors stated in 1993:[6]

> Ignoring the helium-heat relationship (Table 2 in Figure 1), the simple yes or no detection of helium in 8 out of 8 experiments producing excess power and the absence of helium in 6 out of 6 experiments not producing excess heat (1 in D_2O, 5 in H_2O) implies a chance probability of only $(1/2)^{14} = 1/16384$ or 0.0061%.

(Essentially the same wording appears also in ref 2.)

In addition to obvious discrepancies in the two statements, the helium–heat relationship cannot be ignored. It is crucial

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A) 1991

Table. 1. Helium Production During D_2O Electrolysis.

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

[a] $i = 250$ mA/cm^2. All other experiments used $i = 200$ mA/cm^2.
[b] Possible calorimetric errors due to low D_2O solution levels. No ^{3}H was detected. Mass spectrometer always at highest sensitivity.

B) 1993

Table 2. Helium Production During D_2O Electrolysis: Revised Detection Limits.

Sample	P_{EX} (W)	X	^{4}He Atoms/500 mL[a]
12/14/90-A	0.52b	1.20[b]	10^{15} (large peak)
10/21/90-B	0.46	1.27	10^{15} (large peak
12/17/90-A	0.40[b]	1.19[b]	10^{14} (medium peak)
11/25/90-B	0.36	1.15	10^{15} (large peak)
11/20/90-A	0.24	1.10	10^{14} (medium peak)
11/27/90-A	0.22	1.09	10^{15} (large peak)
10/30/90-B	0.17	1.12	10^{13} (small peak)
10/30/90-A	0.14	1.08	10^{13} (small peak)
10/17/90-A	0.07	1.03	$< 10^{13}$ (no peak)
12/17/90-B	0.29[b,c]	1.11[b,c]	$< 10^{13}$ (no peak)

[a] No ^{3}He was detected. Mass spectrometer always at highest sensitivity.
[b] $I = 250$ mA/cm^2. All other experiments used $I = 200$ mA/cm^2.
[c] Possible calorimetric errors due to low D_2O solution levels.

Figure 1. Juxtaposition of tables published in (A) 1991[3] and (B) 1993[6] by Miles et al. showing data from the same experiments. P_{EX} is calculated excess power and X is the ratio of measured calorimetric heat rate to calculated heat rate. Discrepancies are discussed in the text. The 10-fold inflation of helium-4 detected from 1991 to 1993 is based on a "revised detection limit of approximately 10^{13} atoms/500 mL." [6] Note that no estimates of statistical or systematic errors are provided. (A: Reprinted from ref 3. Copyright 1991 SIF. B: Reprinted from ref 6. Copyright 1993 Universal Academy Press.)

to the claims of unambiguous correlation between excess power and ^{4}He production. The data show the obvious problem that runs producing more "excess heat" do not always show more "helium production," so that *quantitative* agreement between heat and helium generation is lacking. This is a warning that must not be ignored. If ^{4}He is detectable at 10^{13} atoms/500 mL, why can it not be quantitated at a concentration 2 orders of magnitude higher?

Another way of viewing the ^{4}He data is that eight of ten experiments done in 1990 showed ^{4}He to be present while zero of five experiments done in 1991 showed ^{4}He to be present.

Recent experiments likewise show little if any ^{4}He.[8] Are they simply getting better at keeping ^{4}He out? To be valid, controls must be interspersed randomly in time with noncontrols, or, even better, run in parallel. N_2-filled flasks showed diffusion of 3.2×10^{12} atoms of ^{4}He per day,[4] giving 1.9×10^{14} atoms in 60 days, nearly twice the claimed helium production rate shown in Figures 1 and 2. Miles has argued that H_2 (or D_2) prevents diffusion of ^{4}He into the flasks.[4] But studies at Rockwell showed that atmospheric helium enters glass flasks even when hydrogen is present inside the flask [N. Hoffman, private communication].

A) 1991

B) 1993
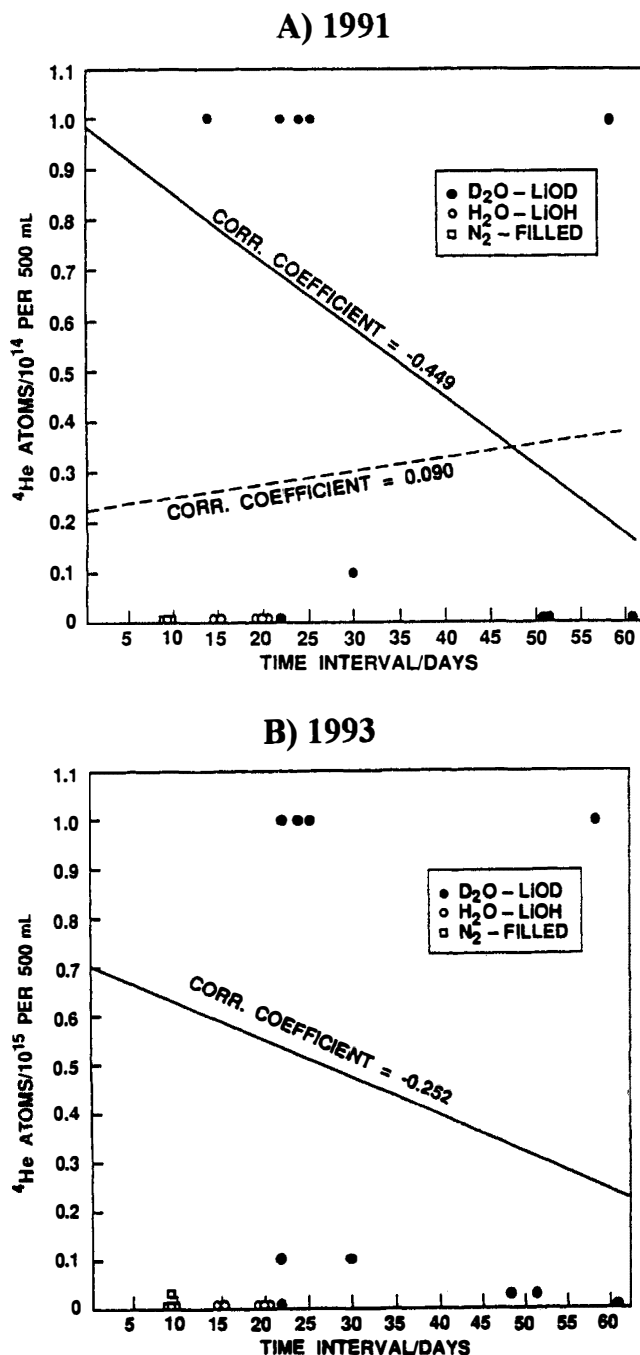
Figure 2. Plot showing data points representing amounts of helium measured versus the storage time interval between gas collection and helium analysis. Note the differences in plotted points between A and B, although the plots represent the same data as shown in Figure 1. Note that there are no data points which lie between 10^{13} and 10^{14} helium-4 atoms/500 mL in A or between 10^{14} and 10^{15} in B. The straight-line fits provided by Miles et al. to these scattered points with the quoted three-figure precision of the correlation coefficients are a bizarre application of statistics. Note the absence of error bars. (A: Reprinted from ref 3. Copyright 1991 SIF. B: Reprinted from ref 6. Copyright 1993 Universal Academy Press.)

Moreover, both arguments of statistical significance cited above leave out run 12/17/90-B, which shows more heat than three other supposed heat-producing runs, but which shows *no* helium-4 at all. Clearly, including this run would dramatically *decrease* the purported significance of the excess-heat/helium production claims and remove completely the alleged one-to-one correspondence of heat and helium production. There is no apparent justification for including run 12/17/90-A in the calculation in 1993 (thus improving the alleged statistical

significance over the 1991 calculation) when run 12/17/90-B, which had the same problem of possible calorimetric error, was excluded.

The statistical significance of the data is meaningless without information on associated uncertainties and if all runs are not treated equally. These steps were clearly not taken. The lack of agreement between the amounts of helium detected and the amount of excess heat generated must be reconciled with the alleged one-to-one correspondence between excess heat and helium-4 production. Finally, the observation of helium-4 in four out of ten nitrogen-filled control flasks[4] must be included for consistent and fair treatment of the data.

Much of the above could be argued to be mistakes in presentation (which we all are prone to), but data purporting to "unambiguously show" [2] a significant new phenomenon such as "cold fusion" must meet a higher standard than is present in Miles' papers.

Contamination from atmospheric helium-4 cannot be strictly ruled out because the concentration of helium-4 detected never exceeds that in the laboratory air. Miles et al. acknowledge that "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." [3] Escape of helium contained in the glass must also be considered, an effect which led Paneth and Peters to their erroneous claim of helium production in hydrogen-loaded palladium nearly seventy years ago.[10] Paneth and Peters retracted their claims of helium production in 1927,[10] as did Pons and Fleischmann in May 1989.[11]

With such small helium concentrations observed, a prosaic origin of the helium should be suspected. Helium-4 is prevalent in the laboratory environment, as Miles and co-workers admit: "because of the use of helium-cooled nuclear magnetic resonance instruments and helium-filled glove-boxes in the building, the helium content of the laboratory air can be significantly higher than 5.22 ppm." [4]

In light of these uncertainties, we remain unconvinced that the published data are strong enough to support the conclusion "our electrochemical experiments unambiguously show a direct correlation between the time of generation of excess enthalpy and power and the production of ^{4}He." [2]

Two very recent papers[6,12] have attempted to answer some of the above criticisms. One of these papers[6] now claims an even higher detection limit for ^{4}He of 3.10×10^{13} atoms/500 mL in the glass flasks used in previous studies. The other study[12] used 500 mL metal flasks to collect electrolysis gases. Five control experiments, four in D_2O + LiOD and one in H_2O + LiOH, all run at 500 mA "yield a mean value of 4.4 ± 0.6 ppb" ^{4}He with extreme values at 4.9 and 3.4 ppb. The paper states that "no excess power was measured" for these "controls", but no values for excess powers with attendant error estimates are provided to substantiate this claim and to allow comparison with experiments where a small excess power is claimed. (Thus making the latter noncontrols.) Note that designation of an experiment as a "control" is done after the experiment is run, not before. Gases were collected and analyzed for five experiments in D_2O + LiOD electrolyte that produced putative excess heat rates from 30 to 60 mW and excess ^{4}He ranging from 1.0 ± 1.6 to 5.3 ± 1.3 ppb. The four of these experiments producing the highest excess heat rates and excess ^{4}He were run at 400 mA. Only one was run at the same current as the controls, and that run produced both the lowest excess heat rate and excess ^{4}He. Neither result is significantly different from controls. Since the excess heat rate and excess ^{4}He for the other four experiments are not positively correlated, the hypothesis

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of a correlation between excess heat rate and excess ^{4}He remains unproven. Furthermore, the amount of excess ^{4}He found is less than 1% of that required to account for the excess heat by "cold fusion". Also, as shown later, the error in the excess heat rate measurement is much greater than the 20 mW assumed in ref 12, and therefore none of the excess heat rate data are significantly different from zero. If the excess heat rate is invalidated, then the claimed qualitative correlation between positive observations of excess heat and excess ^{4}He must also be fortuitous, spurious, or covariant. The data treatment by which Miles arrives at the conclusion that the probability of his hypothesis being wrong is only 1/134,217,730 is severely flawed because of the unsubstantiated data selection.

Claims of Excess Heat Production

In their critique of experiments by Lewis, Williams, Albagli, Wilson and others,[1] Miles et al. challenge "questionable cell calibration procedures" and varying calorimetric cell constants. But the same problems are present in their own experiments.

Miles et al. used the following equation to evaluate excess enthalpy:[2]

$$X = \text{power out/electrolysis power} = K\Delta T/I(E - E^\circ_H) \quad (1)$$

where K is the calorimetric cell constant, ΔT is the temperature difference, E is the cell voltage, E°_H is the thermoneutral potential, and I is the current through the cell. Excess power (enthalpy) is claimed when $X > 1$. Open cells were used with an assumed thermoneutral potential of 1.53 V for the D_2O cells and 1.48 V for the H_2O controls.

Published results are presented in Figure 1. The highest excess power, 0.52 W, was observed on December 14, 1990. Since that date four years ago, Miles et al. have not been able to reach even this low level of excess power.[6,8,12] Moreover, the first 12 days of data for this run have not been published, although the same (partial) data plot has appeared in several publications[2-6] and we have asked for disclosure of all the data. Disclosure of these data is important since X may have been <1 early on, showing possible energy storage in the cell (e.g., reactions of PdD_x[13] and phase transitions at 19 and 30 °C in Teflon[14]), so that the *net* total energy for the run may be consistent with zero. Figure 6 of ref 5 shows just such a situation with light water cells where a *negative* excess heat was observed for the first 12−16 days.

The calorimetric cell "constants" reported in 1990[5] show significant variations: 0.138 to 0.145, 0.132 to 0.138, 0.133 to 0.137, and 0.135 to 0.141 for the four cells. Moreover, calibrations were done before and after long runs, not during runs. It is not valid to claim an *accuracy* based on the standard deviation of these values, since at any time the applicable value may be at an extreme. Thus, the spread of about 4.5% is more descriptive of the ability to accurately measure an absolute heat rate at any given time. Also, different thermistors gave calibration constants differing by 5%. Which is the accurate value? If the X value is moved from 1.00 ± 0.05 to 1.05 ± 0.05, four of the eight claims of excess heat would disappear. The results for H_2O (blank) cells given in Figure 6 of ref 5 show positive excursions of X as large as 15% and negative excursions as large as −20%. Why are these not considered as significant as the smaller excursions observed with D_2O cells? Although the long-term mean of X is different for H_2O and D_2O cells, this difference is meaningless because of fluctuations in the calibration constant. Miles's results simply illustrate the problem of sorting calorimetric errors from real effects in a poorly designed calorimeter. Since large fluctuations in X are

found for both H_2O and D_2O runs in the 1990 data,[5] the authors should have evaluated K values frequently during the runs in order to verify stability. This was not done.

There are numerous other problems with the calorimetric measurements. The calorimeters used by Miles are isoperibol (i.e., constant environment) heat conduction calorimeters. The principle of heat measurement in this type of calorimeter is Newton's law of conductive heat transfer, i.e., the rate of heat flow to or from the calorimeter must be directly proportional to the temperature difference between the calorimeter and the surroundings. Measurement of the temperature difference across the heat flow path between the calorimeter and surroundings and proper calibration thus provides a means for measurement of heat flow. The design criteria required to obtain accurate results with heat conduction calorimeters were developed more than fifty years ago by Tian, Calvet, and co-workers[15] and have since been refined and polished by many other workers. The most fundamental design criterion is that all heat leak paths between the calorimeter and surroundings must have constant thermal conductance. A second criterion required for accurate operation of the calorimeter is that as large a fraction of the heat as possible must pass through the path on which the temperature difference is measured, and further, this fraction must remain constant. Miles' calorimeters meet neither of these criteria.

Miles et al.[1] describe two calorimeter designs, the first consisting of "a Thermos flask (Model 3700) containing the electrochemical cell as well as added insulation", and the second, claimed to be more accurate, "consists of a polyethylene bottle ($d = 7.5$ cm) fitted with a large glass tube ($d = 3.1$ cm) and packed with insulation. The electrochemical cell ($d = 1.5$ cm, $L = 15$ cm) was positioned within the large glass tube which contains water that serves as a heat-transfer medium. The temperature inside the calorimeter is measured to within ±0.01 °C by two thermistors positioned at different levels on the surface of the electrochemical cell." The constant temperature bath around the calorimeters is described only as "B. Braun Thermomix Model 1460 ... set at 27.50 °C" with no indication of how stable the temperature is or if there are temperature gradients present in the bath. Thus, we do not know how stable this half of the temperature difference measurement is, nor do we know the stability of the heat conduction paths to the bath. The other half of the temperature difference is measured with the thermistors in the water-filled "gap" (Miles' terminology). The use of thermistors, which are self-heated sensors, in an unstirred liquid will give rise to temperature drifts because of temperature gradients in the water and may lead to occasional large temperature excursions if the temperature inversion in the water (admitted to in an early paper[5]) is discharged by convection.

The heat leak paths from Miles' calorimeters are neither well-defined nor constant with time or cell conditions. Miles et al.[1] recognize part of this problem when they state "the level of the electrolyte exerts a major calorimetric effect. ... This effect limits the accuracy to about ±10% in our studies using the Dewar-type cells" and "heat flows out of the top of the cell as well as into the constant-temperature bath". The calorimeter design with the water-filled gap is an attempt to ameliorate this problem. However, there are multiple heat leak paths that carry major fractions of the heat transferred in both designs. Furthermore, these paths have greatly different time constants. Miles et al.[1] recognize part of the consequences of this problem in their conclusion that "there is never any steady state for either the cell temperature or the cell voltage" but fail to quantify the consequences in the estimated accuracy of their heat measure-

ments. Accurate heat rate measurements by heat conduction calorimetry can only be made in a steady state unless corrections are made for the time response of the system. Such corrections, which can be very large, can only be made if all significant time constants are known and the system is properly calibrated. Miles et al. estimate a single time constant of 25 to 30 min for their system,[1,2] but it is clear from the details of the design that there must be several more, some of which must be several hours long; see Figure 2 in ref 1.

There are numerous other potential problems with the calorimetric measurements described by Miles et al.[1-8] For example, in none of these publications is the calibration heater fully described, other than that it is a "20 ohm resistor".[5] There is no indication of any precautions taken to ensure complete delivery of heat from the heater to the calorimeter, to ensure negligible heat generation in the heater leads, or to ensure accurate voltage and current measurements. Details of the calibration procedure are likewise not given. How long was the heater run? What does the calorimeter response look like during calibration runs? Was the expected heat output from electrolysis ever duplicated with the heater? Thus, the calorimetric measurements of Miles and co-workers are far from compelling in their accuracy.

We have found no example of a report of excess heat by workers using commercially available calorimeters with proven designs. Yet several brands of heat conduction and power compensation calorimeters suitable for "cold fusion" studies are available. In their calorimeter designs, Miles and co-workers fail to incorporate more than fifty years of accumulated wisdom concerning how to make accurate heat measurements.

Another possible source of error in the papers of Miles et al. lies in the tacit assumption embedded in eq 1 that there are no reactions of the deuterium and oxygen gases produced in the cell, i.e., that Faraday efficiency is 100%. In the denominator of eq 1, the term $IE°_H$ represents the electrical power consumed in decomposing the D_2O into D_2 and O_2. In subtracting this power from the input electrical power, it is assumed that there is no recombination of D_2 with O_2 by any mechanism. If recombination occurs in the cell, this provides a prosaic source for excess heat. Miles and co-workers justify the assumption of 100% Faraday efficiency thus:[9]

> There is no evidence for any recombination when a palladium rod cathode is used that is fully immersed in the D_2O solution.

In a more recent paper, Miles et al.[1] acknowledge the problem of current efficiency by including a factor in eq 1 to correct for a current efficiency less than 1:

> The current efficiency for D_2O electrolysis (γ) should always be measured to substantiate any claims for excess power.

Their published claim to have measured current efficiency states[2]

> Actual measurements of the gas evolution rate by the displacement of water yielded 6.75±0.25 mL/min for cell A and 6.69±0.15 mL/min for cell B. These data add to the substantial evidence that excess enthalpy effects cannot be explained by the recombination of D_2 and O_2 gases within the cell.

But Miles et al. would have had to measure the amount of recombination in *each* experiment in order to truly ascertain if any "excess heat" were present. Clearly, this needs to be done

during the time period when excess heat is claimed, not in separate tests. Furthermore, if the stated error limits on gas evolution rates[2] are 1 standard deviation, then there is still a high probability of a single measurement having up to 10% of the gases recombined. Recombination is thus a possible explanation for X values between 1.0 and 1.1 based simply on the statistical distribution of the measured data.

In another paper, Miles purports to have avoided recombination because "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."[3] But this does not solve the problem. D_2 and O_2 both diffuse rapidly through Teflon, so that recombination could indeed have occurred on the leads in the cell headspace. (In fact, Teflon is used as the membrane material for oxygen electrodes.) Moreover, recent experiments at BYU clearly demonstrate that recombination *does* occur even when both electrodes are fully immersed in the electrolyte.[16] This has been shown for both Ni/H_2O, K_2CO_3/Pt and Pd/D_2O, $LiOD/Pt$ cells. Indeed, we have found up to several hundred percent "excess heat" as calculated by eq 1, which went to zero when recombination was inhibited. By comparison, Miles et al. observed a maximum of 27% excess heat. Thus, *apparent* excess heat can be obtained when recombination is not carefully excluded during electrolysis runs.[16] Where is the evidence that recombination is not occurring during periods of excess heat generation?

Based on Miles' data, the null hypothesis that excess heat arises from calorimetric errors or reduced Faraday efficiency cannot be excluded.

Claims of Nuclear-Product Detection

The nuclear-product detectors used by Miles et al. are described as follows:[2]

> A neutron survey meter (Ludlum Model 15) was always kept close to the water bath containing the two electrochemical cells. A Geiger-Mueller (GM) alpha-beta-gamma detector with a thin end window (Ludlum model 44-7) was positioned about 20 cm from the tops of the electrochemical cells and connected to a scaler ratemeter (Ludlum model 2200) and a printer (Casio HR-8A). Dental X-ray film (Kodak ultra-speed, DF-58) placed near the outside of the electrochemical cells was also used to detect any radiation. ... Indium (d=0.25 mm, 2.2 g) and gold (d=0.5mm, 14 g) foils mounted at the surface of the electrochemical cells were used in attempts to detect any sustained neutron emission rates of 10^4 neutrons/s or higher.

None of these detectors provides particle identification or accurate energy information. Use of such crude detectors does not provide the level of scientific proof required to establish "cold fusion". As we shall see, there are also unexplained discrepancies in the data from these instruments.

Miles et al. provide data from their Geiger counter in a recent paper.[6] The mean background rate was stated to be 31,296 ± 275 counts per 12 h with a maximum of approximately 38,000 counts per 12 h observed on December 15, 1990. This maximum is calculated to be 27 standard deviations, i.e., $(38,668-31,296)/275 = 27$, above background. However, this calculation fails to combine the statistical errors in the foreground and the background rates. Moreover, their claim of statistical significance fails to account for large drifts normally

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encountered with a Geiger counter. A large ratio is significant only when systematic instrument fluctuations have been excluded.

If the data point of 38,668 counts/12-h-period is taken at face value, an extremely large total source radiation is implied. A maximum Geiger counter rate of $(38,668-31,296)/12$-h, or approximately 600 counts per hour, was reported. The counter was located 20 cm from the electrolytic cells, giving a geometrical acceptance factor of approximately 0.006. Since the neutron detector showed no signal,[6] and 20 cm through glass, D_2O-electrolyte, and air is too far for betas, alphas, or other charged particles, only gammas are left to excite the Geiger counter. The intrinsic efficiency of a Geiger counter for gammas is roughly 0.001. Combining geometric and detection efficiencies with the observed rate, a source rate of 10^8 gammas per h is found, even without accounting for attenuation. This rate is sufficient to produce counts in the safety monitor (Ludlum Model 15) since it is sensitive to gammas at this level, but this detector (Miles states) showed no response at all.[6] The discrepancy between the two counters suggests that fluctuations in the Geiger counter led to a spurious signal.

Compelling evidence for gamma ray emission requires data from a reliable (e.g., germanium) gamma spectrometer, rather than a Geiger counter. Even so, Geiger counter data would be more persuasive if more than one detector had shown signals simultaneously, or if lead and other filters had been placed between detector and cell when an apparent signal was evidenced. But these obvious steps were not used to test the validity of the signal.

Sensitive neutron detectors are available[17] but were not used in the studies by Miles and co-workers. In any case, no significant neutron signals, including secondary neutrons, were found by Miles et al.[2]

In an effort to detect X-rays or other radiation, Miles et al. used dental X-ray film.[2,3] The results are not convincing because artifactual fogging can be caused by mechanical pressure and various chemical vapors.[17] Hence, data from X-ray spectrometers (primarily germanium and SiLi detectors) is considered requisite evidence for X-rays; yet *no* cold fusion experiment anywhere has produced an X-ray spectrum showing characteristic (Pd or Ni, etc.) lines.[17] These null results are compelling since *any nuclear* process occurring in a metal at rates sufficient to produce excess heat must also generate copious X-rays due to excitations in the metal lattice.[17] In 1993, we offered Miles and co-workers the use of one of our sensitive X-ray spectrometers (one of which is readily portable and could be used in his own laboratory). Unfortunately, he did not respond to our offer.

Theoretical Considerations

The authors use the following reaction as a "basis for an estimate of helium production":[2]

$$^2D + {}^2D \rightarrow {}^4He + 23.8 \text{ MeV (lattice)}$$
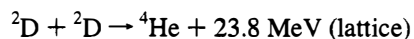
i.e., the 23.8 MeV of energy released in this d−d fusion reaction is assumed to be absorbed by the palladium metal lattice. But there are constraints imposed on transfer of energy to the lattice without formation of energetic particles. Following a nuclear reaction, the energy released can be transferred a distance (R_{max}) limited by the speed of light (c) and the uncertainty principle (ignoring small factors):

$$R_{max} = ct = \hbar c/E = 197 \text{ MeV·fm}/23.8 \text{ MeV} = 10^{-14} \text{ m} =$$
$$10^{-4} \text{ Å}$$

Note that E is of the order of MeV for nuclear reactions, specifically 23.8 MeV for the fusion reaction posited by Miles et al.[2] Since the metal lattice spacing is more than an angstrom, the nuclear energy *cannot* be transferred to the lattice as hypothesized without violating speed-of-light constraints. Furthermore, conservation of momentum requires that most of the energy be carried by the lighter particle rather than by the lattice, as indeed is observed in the Mossbauer effect.

In muon-catalyzed fusion experiments, d−d fusion produces t + p or ^3He + n in nearly equal proportions;[18] ^4He is not detectable (branching ratio $\approx 10^{-6}$).[18] Yet Miles and co-workers claim that ^4He is produced in the absence of detectable tritium, ^3He, or neutrons.[2-6] Hence, their claim is inconsistent with the results of experiments involving real, verified, muon-catalyzed cold fusion.

In another theoretical foray, Miles states that[19]

> For materials at very high pressures, theoretical equations suggest that cations lose their charge at 10^{17} atmospheres and unite with electrons in the plasma with emission of neutrinos. Since this would neutralize the charge of deuterons, the coulombic barrier would collapse and fusion could readily occur.

Miles overlooks major problems with his explanation. (a) An actual pressure of 10^{17} atm cannot be reached in palladium in an electrolytic cell,[20] and (b) should an electron capture occur on a deuteron with release of a neutrino as Miles hypothesizes, there are no longer two deuterons present so that d−d fusion obviously cannot occur.

Conclusions

In response to a request by Miles et al., we have reviewed their published papers purporting to show ^4He, X-ray, and excess power production in Pons−Fleischmann-type electrolytic cells. We find the data do not support the conclusion that a nuclear reaction is the source of the putative excess heat. The claimed correlation between ^4He and excess heat is weak to nonexistent and qualitative conclusions are overstated. Putative excess heat observed could be the result of calorimetric errors and recombination of D_2 and O_2 within the cell. Nuclear detection methods are far from adequate, and the claimed results are inconsistent. Miles et al. treat within-experiment data as independent observations, thus making it appear that they have much more data than were actually obtained. Far too few proper control experiments have been done. Without proper and sufficient controls, the causal inferences Miles et al. have made are untenable.

Recent remarks of Miles et al. support our conclusion that excess heat and helium production in Pons−Fleischmann-type cells have a prosaic origin:

> Reproducibility remains a major problem in defining these effects.[6]

> Because helium is present in the atmosphere (5.22 ppm), it is difficult to convince everyone that the ^4He measured in the electrolysis gas is a product of a fusion reaction within the cell. It is indeed a very challenging experimental problem to clearly establish the production of ^4He from Pd/D_2O electrolysis cells. This situation is compounded by difficulties in obtaining large excess power effects in these experiments.[8]

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Clearly, there is no compelling evidence that cold fusion is the source for "excess power" observed in electrolytic cells. Experimental artifacts cannot be excluded as the sources of both the excess power and ^{4}He claimed by Miles and co-workers. The dental X-ray films and Geiger counters likewise are crude detectors and do not provide compelling evidence for nuclear reactions occurring in electrolytic cells. Because many of the criticisms of Miles' work are also applicable to others' claims of excess heat in Pons–Fleischmann-type "cold fusion" experiments, we do not find the data to be compelling proof of any nuclear phenomenon in spite of the number of positive claims for excess heat that have appeared in the literature.

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COMMENTS

Reply to "Examination of Claims of Miles et al. in Pons−Fleischmann-Type Cold Fusion Experiments"

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Introduction

This paper is a response to S. E. Jones and L. D. Hansen,[1] who critically examined our claims of excess heat and helium-4 production during electrolysis of the Pd/D_2O + LiOD system.[2−5] Many of the allegations regarding our work have been discussed in previous publications.[2−6] We have also critically examined the basic principles and problems in measurements of excess power during Pd/D_2O + LiOD electrolysis in isoperibolic calorimeters.[7] The claim by S. E. Jones and co-workers[8] that faradaic efficiencies less than 100% can account for reports of excess heat in cold fusion cells is not valid at the high current densities ($j \geq 100$ mA/cm^2) required for these experiments.

Excess Heat Production

The calorimetric results reported by our laboratory have been used to support both sides of the scientific controversy regarding anomalous effects in deuterated metals. Our first set of experiments conducted over a 5-month period (April−September 1989) produced no significant evidence for any excess enthalpy production.[9] The mean value for the ratio of heat out to joule heat in was $X = 1.00 \pm 0.04$ in our most accurate calorimetric study.[9] These early experiments at China Lake were listed in the Energy Research Advisory Board report to the U.S. Department of Energy as one of the groups *not* observing excess heat.[10] It is difficult to explain why our early calorimetric studies reporting no excess heat[9,10] are acceptable to critics of this field when later studies, that are actually more accurate, are judged to be in error.

Research groups from MIT, CalTech, and Harwell laboratories also reported no evidence for excess heat,[7,10] thus greatly impacting the general scientific opinion regarding this field in 1989. All three groups discontinued their experiments after only a few months of investigation. We continued to investigate other palladium samples and eventually observed significant evidence for excess enthalpy from the use of Johnson−Matthey palladium rods.[2] In retrospect, it would be impossible for any research group to adequately investigate the multitude of variables involved with this field in only a few months. These variables range from the palladium metallurgy to the D_2O purity, the type of electrolyte and concentration, the electrochemical cell, the electrode arrangement, the type of calorimeter, proper scaling of the experiments, the handling of materials, the current

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densities used, the duration of the experiments, the loading of deuterium into the palladium, the use of additives, and so on.

As should be expected, our calorimetry has improved with time. An early version had glass tubes containing the thermistors that protruded considerably above the tops of the cells.[2] Although the effect of these thermistor tubes was not apparent when the room temperature was stable, cooler weather later produced greater fluctuations in room temperature and unstable thermistor readings. This was especially apparent in a water control study (Figure 6 of ref 2). In the following experiments, the thermistor tubes were made flush with the cell top, resulting in much more uniform measurements. Although Jones and Hansen[1] focused considerable attention on Figure 6 of ref 2, they ignored our explanation and correction for this effect (see pp 245−246 of ref 2). A dramatic improvement in the calorimetric stability is seen in the experiment following the H_2O control study (see Figure 7 of ref 2) where the single tail *t* test for excess enthalpy easily exceeds the 99.95% confidence level (see Table 2 of ref 2). Many of these issues were thoroughly discussed in a previous debate with S. E. Jones.[11]

The accuracy of our calorimetry is illustrated in Figure 1 which features one of many experiments that never displayed any evidence for excess power. The ratio, *X*, of output power to input power remains close to unity. All measurements of excess power were within 0 ± 40 mW for the entire experiment. Approximately 70% of our experiments never displayed any evidence for excess power and served as controls for our calorimetry. In June of 1995, Roger M. Hart, an expert in the design, construction, and testing of calorimeters, examined our calorimetric design and agreed with our stated error range of ± 20 mW or $\pm 1\%$ of the input power, whichever is larger.

A major criticism presented by Jones and Hansen[1,11] of our calorimetry is the variation of the calorimetric cell constants over various experiments. For example, K_1 ranges from 0.135 to 0.141 W/°C over four separate experiments that yield a mean of 0.138 ± 0.003 W/°C (see Table 3 of ref 2). Roger Hart pointed out that this criticism by Jones and Hansen is not valid since all cell components are repositioned in each experiment. The relative positions of the anode and cathode electrodes and of the two thermistors vary somewhat with each new cell assembly; thus, the slight variation in the calorimetric cell constants in different experiments is expected. The many experiments that produced no excess enthalpy, such as shown in Figure 1, indicate that the calorimetric cell constants do not change during an experiment.

Many experiments have proved that the recombination of D_2 and O_2 electrolysis gases does not occur to any significant level for typical cold fusion studies using high current densities and solid, fully submerged palladium cathodes.[4,12] Some scientists, however, prefer to ignore this evidence and continue to claim that the excess heat effect can be explained by faradaic efficiencies less than 100% ($\gamma < 1$).[8] The recombination effects for Ni and Pd cathodes reported by Jones et al.[8] used current densities of only 1−2 mA/cm^2. Such studies are irrelevant since excess heat effects for the Pd/D_2O system require a threshold current density of about 100 mA/cm^2 or higher. This requirement of high current densities was reported by M. Fleischman

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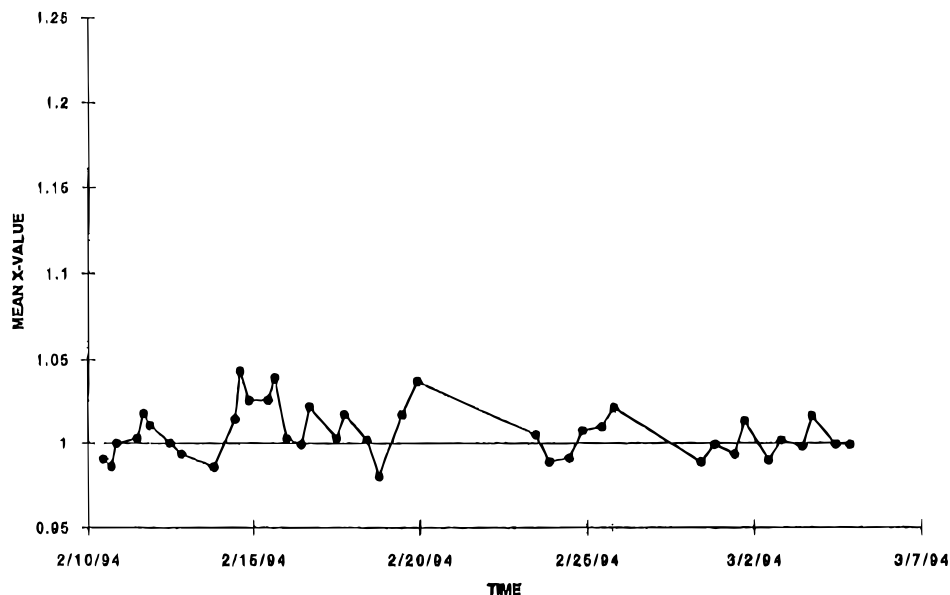
Figure 1. Ratio, *X*, of the calorimetric output power and the electrochemical input power for a palladium sheet cathode. No significant excess power was observed.

et al.[13] in 1990. Lowering the current density in water electrolysis experiments will always decrease the current efficiency due to the slower gas evolution that allows the product at one electrode to more readily invade the vicinity and react at the opposing electrode. Furthermore, the current fraction consumed by the electrode reaction of impurities becomes larger at smaller current densities. Contrary to the comments by Jones and Hansen,[1] we always measured the current efficiency at the time of collection of an electrolysis gas sample for helium analysis. This was done volumetrically by measuring the rate of the displacement of water by the electrolysis gases.[4] For all the runs that appeared in the original table reproduced and criticized in Jones and Hansen[1] as Figure 1, the volume of gases evolved was as expected for no recombination.

Several other measurements and observations provided secondary checks for any recombination of D_2 and O_2 in our experiments. The volume of D_2O added to replenish the cell was always recorded to provide another test for any significant recombination effects. Furthermore, the rate of the electrolysis gases passing through the oil bubbler could always be directly observed. If recombination of D_2 and O_2 within the electrolysis cell occurs, this would slow or even stop the evolution of gases through the bubbler.

There is only one group of experiments where recombination was detected in our electrolysis experiments over a 6-year period. These studies all involved the codeposition method reported by Szpak et al.[14] where palladium metal is deposited from a D_2O solution containing 0.05 M $PdCl_2$ and 0.3 M LiCl onto a copper cathode in the presence of evolving deuterium gas. This method reportedly produced excess enthalpy, tritium, and emanating radiation.[14,15] The deposition of palladium from D_2O solutions offers the possibility of generating a high-purity cathode material that is simultaneously loaded with deuterium. In our experiments, however, this palladium deposit was often dendritic in nature. Hence, the palladium became detached from the electrode, floated in solution, and adhered to the cell wall above the D_2O level. This finely divided palladium acted as an excellent catalyst for recombination in the gas phase; hence, these codeposition experiments sometimes resulted in loud explosions. There was also evidence that the dendritic palladium deposits occasionally contacted the anode, thus allowing some

of the current to pass directly through the cell without producing any electrolysis.

The reaction or recombination of the D_2 and O_2 electrolysis gases or any cell shorting could always be readily detected in our codeposition experiments.[16] For example, there were always obvious changes in the rate of gas flow through the oil bubbler. The extent of these effects was determined by measuring the current efficiency (γ) for the D_2O electrolysis. This was done by volumetrically measuring the rate of evolution of the $D_2 + O_2$ electrolysis gases. The resulting γ can be easily applied to the calorimetric equations to correct for any apparent excess enthalpy produced by recombination or other reactions of the electrolysis gases.

A typical codeposition experiment where significant recombination or dendritic shorting occurs is shown in Figure 2. The apparent excess power reaching levels up to 18% could be readily corrected for recombination or other effects by the simultaneous measurement of the rate of evolution of the $D_2 + O_2$ electrolysis gases. This was used to determine the current efficiency (γ). The corrected values for *X* were then close to unity, and the overall ratio of power out/power in was $X = 1.0005 \pm 0.022$; i.e., no significant excess power was observed after applying the correction for the current efficiency. The results in Figure 2 show that recombination can always be readily detected and easily corrected in our experiments. These results provide further proof that our calorimetric methods are accurate.

Helium-4 Production in Electrolyte Cells

Perhaps the most important point raised by S. E. Jones and L. D. Hansen[1] was that our helium-4 detection limit was first reported as 10^{12} atoms per 500 mL of effluent gases[3,4] and then later increased to 10^{13} ^{4}He atoms/500 mL.[5,6] Our earlier limit was based on measurements at the University of Texas laboratory where 10 mTorr of air in 500 mL of nitrogen gas yielded the observation of helium-4 at the detection limit of the mass spectrometer (see Table 1 of ref 3). We reported that less sensitive detection limits were expected for $D_2 + O_2$ electrolysis gas samples versus N_2 gas samples because of their different absorption properties in the cryofilter that was used to separate D_2 and ^{4}He (see pp 101 and 104 of ref 4). Furthermore, the
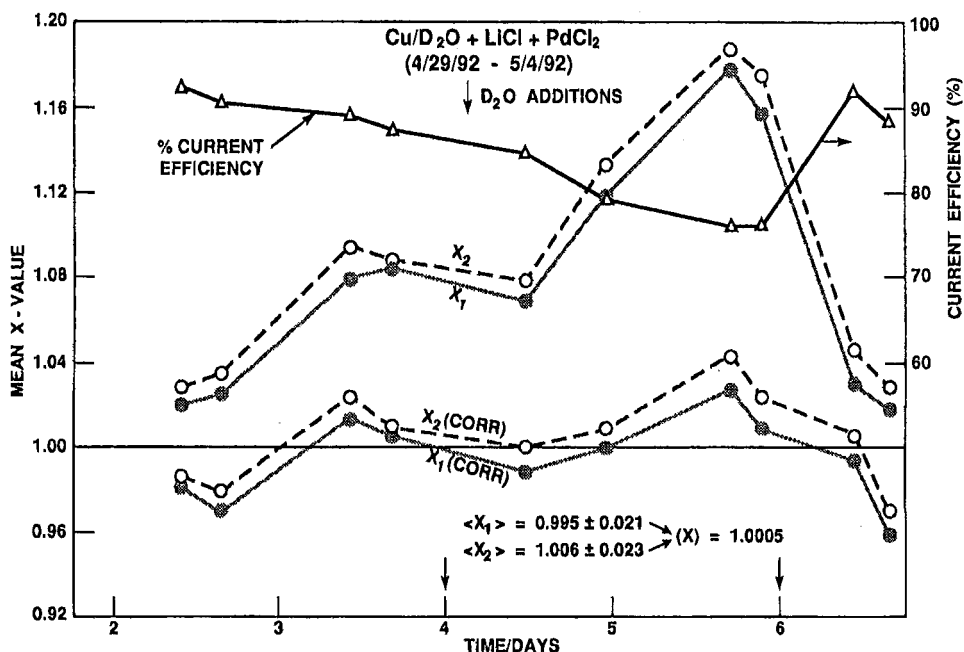
Figure 2. Palladium−deuterium codeposition experiment where the current efficiency is significantly less than 100%. No significant excess power is observed after correcting for the experimental current efficiency (γ).

[4]He content in the chemistry laboratory may have been considerably higher than the normal 5.22 ppm by volume assumed in our calculations.[4] Finally, the assumption that the nitrogen gas did not contain any [4]He atoms may not have been correct, although it was always below the detection limit. Because we did not want to overestimate the amount of helium-4 produced in our experiments, we originally used the conservative estimate of 10^{12} [4]He atoms/500 mL as our detection limit.

Solid evidence that we should have originally reported considerably higher helium-4 production rates was obtained in later studies where the electrolysis gas samples were collected in metal flasks rather than in Pyrex glass flasks and then analyzed by a commercial laboratory.[6] For five control experiments yielding no excess power, the mean background helium concentration in our system was 4.4 ± 0.6 ppb or $5.1 \pm 0.7 \times 10^{13}$ [4]He atoms/500 mL.[6] These values, therefore, accurately define a minimum helium-4 detection limit for our original studies. To clearly resolve this helium-4 detection limit issue, exactly the same procedures and apparatus were used in these experiments except for the replacement of the glass flasks with the metal flasks. This eliminated the diffusion of atmospheric helium into the sample flasks. These quantitative commercial measurements of background helium-4 concentrations in our calorimetric system dictated an upward revision of our original helium reports. It would be absurd to continue to claim 10^{12} [4]He/500 mL (0.1 ppb) as our detection limit when our background helium concentration is accurately determined to be considerably higher.

In retrospect, the higher helium-4 detection limit resolves the issue of atmospheric helium diffusion into our glass flasks and is consistent with the detection limits reported by a commercial laboratory.[5,6] Furthermore, this higher helium-4 detection limit yields helium production rates of $10^{11}-10^{12}$ [4]He s^{-1} W^{-1}, which is the correct magnitude for typical fusion reactions that yield helium as a product.[5,6] The consistent merging of these various results would have been highly improbable if our initial measurements were due to errors or atmospheric contamination. Nevertheless, the revision in our helium-4 detection limit was a major issue raised by S. E. Jones and L. D. Hansen[1] in their

criticism of our work. Our explicit explanations for this change[5,6,11] were completely ignored.

For calculations of our helium-4 production rates, it should be noted that it requires 4410 s to produce 500 mL of electrolyis gases at 528 mA (200 mA/cm^2) for our normal laboratory conditions ($T = 296$ K, $P = 690$ Torr). Therefore, simple calculations show that our results reproduced by Jones and Hansen[1] as Table 2 in Figure 1 yield $10^{10}-10^{12}$ [4]He s^{-1} W^{-1}. Later experiments involving much more accurate helium measurements of our electrolysis gases collected in metal flasks yielded approximately 10^{11} [4]He s^{-1} W^{-1}.[5,6] Therefore, the amount of excess [4]He found can account for nearly all of the excess power observed in our experiments.

Another criticism by S. E. Jones and L. D. Hansen[1] is our exclusion of run 12/17/90-B in calculations of statistical significance.[4] An unusual voltage increase with time for cell B suggested that the D$_2$O level was much lower than normal and not completely covering the electrodes in this cell. Eight days later at the end of this experiment, the D$_2$O level is cell B was 5.1 mL lower than in its companion cell A. These cells initially contained 18 g (17 mL) of 0.2 M LiOD + D$_2$O.[4] We later demonstrated that the low D$_2$O level observed in cell B that exposed the electrodes to the gas phase can yield a false excess heat effect. In early reports,[17] we omitted both cell 12/17/90-A and cell 12/17/90-B from statistical treatments of our heat-helium results since the two cells were run in series. In later reports,[4,5] we included cell 12/17/90-A in statistical arguments since this cell actually had an acceptable D$_2$O level. The questions remains: Do you omit both cells run in series if the experiment is flawed in one cell? If the answer is yes, then you have the earlier result,[17] but if the answer is no, then you have the later results.[4,5] Unfortunately, the sample 12/17/90-A was inadvertently left out in our preliminary report of correlated excess power and helium production (see Table 2 of ref 3).

S. E. Jones and L. D. Hansen[1] contend that our observation of helium-4 in four out of ten N$_2$-filled glass flasks must be included for consistent and fair statistical treatment of our data. We totally disagree because air was deliberately introduced into four of these flasks in order to estimate the helium-4 detection

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limit, and a fifth flask experienced an obvious air leak probably induced by air freight shipment (see Table 1 of ref 3). The only valid controls were four Pyrex flasks filled with boil-off N_2 at the China Lake laboratory and then analyzed at the University of Texas 9 days later. The diffusion rate of 3.2×10^{12} ^{4}He atoms/day measured for our N_2-filled Pyrex flasks[5] and 9 days of storage yields a helium-4 concentration of 2.9×10^{13} ^{4}He atoms/500 mL or 3 ppb due to atmospheric diffusion alone. One N_2-filled Pyrex flask showed the presence of ^{4}He at the detection limit while no helium could be detected for the other three Pyrex flasks (see Table 1 of ref 3). Results for these four N_2-filled Pyrex flasks provide additional evidence that our helium-4 detection limit was considerably higher than 10^{12} atoms/500 mL (0.1 ppb) that we claimed initially.[3,17]

Experimental measurements of the diffusion of atmospheric helium into our Pyrex flasks is presented in Figures 1 and 2 of ref 5. Quantitative measurements by the Rockwell International laboratory clearly show that the amount of helium-4 increases linearly with the flask storage time as predicted theoretically.[5]

Plots of our data presented by Jones and Hansen[1] in their Figure 2 also show the helium-4 concentration versus the Pyrex flask storage time. The later graph (1993) gives the correct data points. The lines drawn in these figures were intended to simply illustrate that there is absolutely no correlation between the helium concentration reported and the flask storage time. The correlation coefficients are actually found to have negative values for either graph rather than the expected positive values; hence, bizarre statistics are encountered for arguments that our helium results are due to atmospheric helium diffusing into our Pyrex glass flasks. Note that the effect of atmospheric helium diffusing into our glass flasks should have been measurable even on an order of magnitude scale if our helium-4 detection limit were actually 10^{12} atoms/500 mL as reported initially. For example, the experimental diffusion rate of atmospheric helium into our Pyrex glass flask yields 2×10^{12} atoms/500 mL after 1 day and 2×10^{13} atoms/500 mL after 10 days.[5]

S. E. Jones and L. D. Hansen[1] report that our designation of an experiment as a "control" is done after the experiment is run, not before. Neither Jones nor Hansen has been in our laboratory; hence, they have no basis for such a statement. Permanent laboratory records always defined the amount of excess power prior to any helium measurements. In general, excess power was consistently produced day after day in experiments that yielded excess helium-4 production, while no excess power was ever detected in experiments that served as controls.[16] In retrospect, helium-4 is probably the only nuclear product that could have remained so well hidden from view over the past 8 years of cold fusion experiments.

There is compelling evidence that the anomalous excess heat measured at our labortory is associated with helium-4 production. For example, 30 out of 33 heat and helium studies yielded either excess helium when excess power was measured or no excess helium when no excess power was present.[16,18] A statistical treatment shows that the probability is approximately one in a million that our complete set of heat and helium results could be this well correlated due to random experimental errors in our calorimetry and helium measurements.[16,18] It is even much more unlikely that random errors could consistently yield helium-4 production rates in the appropriate range of 10^{11}–10^{12} atoms/s per watt of excess power.

Radiation Measurements

Radiation monitoring was imposed upon our laboratory due to safety concerns but was never intended to be a major focus of our program. This is one area where the criticism by S. E. Jones et al.[1] may have some validity. Nevertheless, anomalous radiation was detected by X-ray film exposure,[3,4,17] by the use of several different GM detectors,[5,16] and by the use of NaI detectors.[16] There was never any anomalous radiation when the experiments were not running.

Portable equipment for measuring radiation was available within the Navy;[15,16] thus, our laboratory did not accept the offer by S. E. Jones for the use of his portable X-ray spectrometer. Control studies showed that energies less than 50 keV could not escape from our cell and water bath. The revision of our experiments to optimize the X- and γ-radiation spectrometry would have critically compromised our calorimetry. Appropriate experiments were conducted at another Navy laboratory that yielded evidence for the emission of low-intensity X-rays during cathode polarization of the Pd/D system.[15] These experiments required specially designed cells where the palladium electrode is close to the detector window.[15]

Miscellaneous Issues

S. E. Jones and L. D. Hansen[1] suggest a possible energy storage in the cell where there is a *negative* excess heat early in the experiment. We have never observed any energy storage in cells that produced excess heat. There is no real scope for energy storage in our cells—quite the reverse actually, since if deuterium were to leak out of the palladium, the cell would cool down.

S. E. Jones and L. D. Hansen[1] contend that D_2 and O_2 diffuse rapidly through Teflon; thus, recombination could occur on our anode and cathode lead wires despite our use of thick heat shrinkable Teflon tubing to protect these wires. This effect would certainly be very small and would diminish as the reaction product, D_2O, accumulated at the surface. Furthermore, cell calibrations performed under similar experimental conditions would zero out any such effects. Finally, volumetric measurements of the evolved gases show that no recombination occurs.

S. E. Jones and L. D. Hansen[1] attempt to explain our lack of helium-4 in H_2O-control experiments by suggesting that we were simply getting better at keeping out ^{4}He. They overlook the fact that our very first D_2O sample (10/17/90-A) produced no significant excess power and no detectable helium.[3–5] Later experiments using metal flasks showed that our techniques yielded very consistent results in keeping atmospheric helium out of our system.[6,16]

Several additional statements by S. E. Jones et al.[8] need to be corrected. The thermoneutral potential, E_h, is the cell voltage at which the entropic cooling balances the polarization heating. Its numerical value is $E_h = -\Delta H/zF$, not $\Delta H/F$ as in eq 3 of ref 8, with z indicating the number of charges transferred in one rection step. The correct equation makes E_h invariant with the expression of the cell reaction and the direction of the cell current. At the high current densities used in cold fusion experiments, the cell voltage is always considerably larger than E_h; hence, concerns by S. E. Jones et al.[8] regarding cells operating close to E_h do not apply.

More serious errors by S. E. Jones et al.[8] are found in their presentation of the electrochemical aspects of the cell operation. In particular, they stated that the exchange current density depends on the electrode surface area. The exchange current density always has dimensions of A/m^2 or similar units; hence, it cannot depend on the electrode surface area. Furthermore, there is no such thing as an exchange current density for their reaction 4 in ref 8. This cell reaction consists of the oxidation of hydrogen at the anode and the reduction of oxygen at the

cathode; hence, there are two distinctly different exchange current densities associated with the cell reaction.

Conclusions

Documentation is presented that shows major allegations by S. E. Jones and L. D. Hansen concerning our experiments have already been explained in our previous publications as well as in a 1992 published discussion. The simultaneous measurements of power and the rate of evolution of the electrolysis gases in our experiments prove that faradaic efficiencies less than 100% cannot account for our reports of excess heat. Excess enthalpy for the Pd/D_2O system generally involves high current densities that exceed 100 mA/cm^2; therefore, the report by S. E. Jones et al. of low faradaic efficiencies using current densities of only 1−2 mA/cm^2 is not applicable to our cold fusion experiments. Based on experiments at our laboratory, there is compelling evidence that the anomalous excess heat is associated with helium-4 production. For example, 30 out of 33 heat and helium studies yielded either excess helium when excess power was measured or no excess helium when no excess power was present. The probability of obtaining this result by random errors in our heat and helium measurements is about one in a million. Permanent laboratory records always defined the presence or absence of excess power prior to any helium measurement. The measurement of helium in the electrolysis gas samples at three different laboratories places our rate of helium-4 production at 10^{11}−10^{12} atoms/s per watt of excess power. This is the correct magnitude for typical deuteron fusion reactions that produce helium-4 as a product.

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An Assessment of Claims of Excess Heat in Cold Fusion Calorimetry

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Miles' response[1] fails to adequately address either of the major conclusions of our paper[2] criticizing his work.

1. The "anomalous" radiation and helium-4 observed by Miles are artifacts. Miles' response addresses some of our concerns regarding his radiation detectors. He admits that "this is one area where the criticism by S. E. Jones et al. may have some validity."[1] However, he maintains, "Nevertheless, anomalous radiation was detected by X-ray film exposure, by the use of several different GM detectors [Geiger counters], and by the use of NaI detectors."[1] He did not address our concerns regarding well-documented artifacts in X-ray film[3] such as he used in some experiments or our questions regarding discrepancies between instruments. For example, his Ludlum safety monitor showed no response when his GM detector allegedly showed a signal. We argued that this discrepancy between detectors "suggests that fluctuations in the Geiger counter led to a spurious signal."[2] Only the most reliable, state-of-the-art instruments could establish a new phenomenon such as cold fusion, and Miles et al. did not use such instruments.

Miles et al.[4] posit the following reaction as the source of the helium-4 observed.

$$D + D \rightarrow {}^4He + 23.8\ MeV \quad (lattice) \qquad (1)$$

That is, the 23.8 MeV of energy released in this D−D fusion reaction is supposed to be absorbed by the palladium metal lattice. But this claim is demonstrably wrong. Conservation of momentum and energy requires that most of the energy be carried by the lighter particle (^4He in this case) rather than by the lattice—as is indeed observed in the Mossbauer effect where the emitted particle carries essentially all of the released energy. Miles et al. attempt to turn the observed Mossbauer effect on its head, with the lattice somehow absorbing the lion's share of the energy (and momentum). Just as serious, the nuclear energy cannot be transferred to the lattice without violating constraints imposed by the uncertainty principle and the speed of light.[2] These fundamental arguments do not depend on information obtained from hot-plasma fusion studies. Why are these crucial points ignored by Miles?

2. Calorimetric errors can account for the "excess heat" claimed by Miles et al. The accuracy of Miles' heat measurements depends on the assumption that the temperature measured by a point sensor accurately represents the average temperature of the calorimeter wall. This can only be tested by checking the calorimeter calibration with a standard chemical reaction with a well-known heat effect. Electrolysis is not an acceptable standard reaction. It has now been over 2 years since our critique[2] of Miles' calorimetry appeared, but we have not seen any attempt by Miles to verify the accuracy (as opposed to precision) of his calorimeters. During that time we have done further work[5] that supports the conclusions in our critique of Miles' work. We have built and operated calorimeters similar to Miles' and shown that heat measurements made with such calorimeters are usually precise, but subject to large systematic errors if stirring is inadequate to validate the above assumption. This is particularly true for experiments involving high heat rates such as are obtained at the high currents used by Miles. Furthermore, Miles' response[1] discloses that "all cell components are repositioned in each experiment." It is not clear why this repositioning of "all cell components" is necessary or desirable. However, changes in the calibration constant with repositioning of temperature sensors and other parts in the calorimeter are an indication that Miles' calorimeters are indeed affected by systematic errors stemming from inadequate stirring.[5] Miles says nothing to convince us that such systematic errors are not the source of the apparent "excess heat" observed in his experiments.

Whether $E_h = -\Delta H/zF$ or $-\Delta H/F$ depends on whether the units on ΔH are given in moles or equivalents.

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Reply to "An Assessment of Claims of Excess Heat in Cold Fusion Calorimetry"

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1. My journal publications criticized by Jones and Hansen report only experimental results; hence, theoretical arguments are not germane to this debate. In science, theory guides but experiments decide. Nevertheless, several theories exist for cold fusion that fit nicely with my experimental results.[1,2] I cannot find any experimental errors that explain our radiation and helium-4 measurements.

2. The rate of stirring was carefully considered as a possible error source in our calorimetric experiments. We found that stirring was not a significant error source at currents greater than 100 mA (see Figures 3 and 4 in *J. Phys. Chem.* **1994**, *98*, 1948−1952). Our calorimetric experiments generally used currents of 400−600 mA. We always employed long, narrow calorimetric cells that provide rapid radial and axial mixing of the electrolyte by the electrolysis gas bubbles. In our calorimetric cell designs, the temperatures were measured in an integrating liquid or solid phase surrounding the electrochemical cell. The new experiments reported by Shelton, Hansen, Thorne, and Jones[3] are not applicable to our results since their cell temperatures are measured directly in the electrolyte. Stirring will be inadequate if short, fat calorimetric cells are used as shown in the Figure 1 schematic by Jones et al.[3] F. G. Will[4] reports that the experimental results of Jones et al.[5] on faradaic efficiencies less than 100% (recombination) were obtained at small current densities (0.5−4 mA/cm^2) and that the extrapolation of these findings to the much larger current densities generally employed in cold fusion studies has led Jones et al. to incorrect conclusions. Therefore, $H_2(D_2) + O_2$ recombination must be ruled out as an explanation for excess heat.[4]

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An assessment of claims of 'excess heat' in 'cold fusion' calorimetry

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Abstract

Claims of 'excess heat' from measurements of the heat of electrolysis at several watts of power are largely based on use of poorly characterized, isoperibol, heat-conduction calorimeters with single-point temperature sensors. This paper describes construction, testing, and calibration of a calorimeter of similar design. Heat-conduction calorimeters with single-point temperature sensing and inadequate mixing are subject to large systematic errors resulting from non-uniform heat distribution within the system. Confirmation of electric-heater calibration by a chemical reaction with a well-known enthalpy change is a minimum requirement to insure accuracy. Improper or incomplete calibration is a probable cause for many claims of 'excess heat' in 'cold fusion' experiments. ● 1997 Elsevier Science B.V.

1. Introduction

Claims of nuclear products accompanying excess heat in 'cold fusion' electrolysis experiments have largely been discredited [1-3], but little work has been done to test the claims of 'excess heat'. Continuing claims of excess heat and the untested and poorly characterized calorimeter designs used to generate these claims became the reason for us to reluctantly enter this arena in an effort to determine the validity of observations of 'excess heat'. In the first paper [4] in this series, we used a commercially available, isoperibol, differential heat-conduction calorimeter to demonstrate that many claims of 'excess heat', particularly at low current densities, were the result of assuming 100% Faradaic efficiency when in reality Faradaic efficiencies were much less. Because of the non-linear response at heat rates > 60 mW, experiments in that calorimeter were restricted to relatively low currents and current densities. For work at higher power, EPRI provided a small grant to construct a calorimeter which would fit in our neutron detectors and could accurately measure heat rates up to several watts. Because of its potential utility in other applications, development of this calorimeter has continued even though EPRI withheld further support after being informed of the results of the work done at low power. Obtaining accurate heat rates from the high-power calorimeter proved to be a challenge because of subtle, but large systematic errors associated with mixing and single-point temperature sensing in the calorimeter.

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The governing equation for heat conduction calorimetry is [5]

$$\Phi(t) = G\{\theta(t) + \tau[(d\theta(t)/dt]\} \qquad (1)$$

where $\Phi(t)$ is the rate of heat accumulation by the calorimetric cell and exchange with the surroundings as a function of time (t), $\theta(t)$ the temperature difference between the vessel and surroundings as a function of time, τ the calorimeter time constant, and G the thermal conductance between the calorimeter and the surroundings. Under conditions in which the time constant (τ) is very small or the derivative of the temperature difference $(d\theta/dt)$ is negligible [5] and the surroundings are at constant temperature, Eq. (1) reduces to

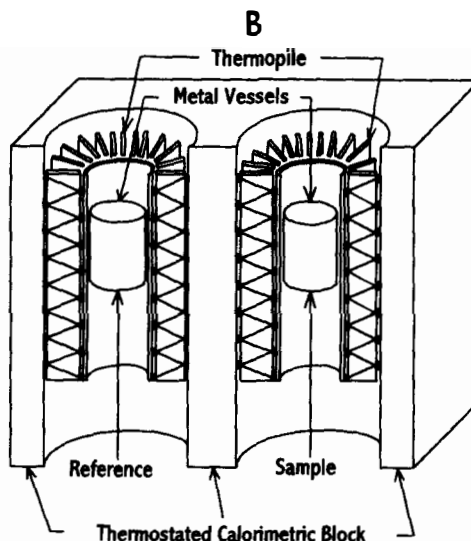$$\Phi(t) \equiv G\theta(t) = G[T_{system}(t) - T_{surroundings}] \qquad (2)$$

where $\Phi(t)$ is the rate of heat exchange with the surroundings as a function of time, $T_{system}(t)$ the average temperature of the surface of the calorimeter vessel, and $T_{surroundings}$ the average temperature of the materials surrounding the calorimeter vessel. Determination of $\Phi(t)$ thus only requires the measurement

of $\theta(t)$ and G, but only if the calorimeter is designed so that Eqs. (1) and (2) accurately describe the thermal behavior of the calorimetric system.

The design criteria for obtaining accurate results with heat-conduction calorimeters were recorded by Calvet et al. [6] over fifty years ago. The thermal conductivity of all heat paths between the cell and its surroundings must be constant or G will vary. The θ measured must accurately represent the actual temperature difference between the calorimeter vessel and the surroundings. The heat-conduction paths must be the same during calibration and measurement. As can be seen in Fig. 1B, commercially available heat-conduction calorimeters that have been proven to perform accurately meet these conditions. These have vessels constructed of a good thermal conductor with a major part of the surface area in contact with a thermopile which also serves as the constant thermal path to the heat sink. Even in these calorimeters, the calibration constant determined by electrical calibration may depend (to a few percent) both on the location of the heater and the contents of the calorimetric vessel [7,8].

A
Uncontrolled Environment
Thermostated Water Bath
T_{surr} T_{sys}
Insulated Vessel
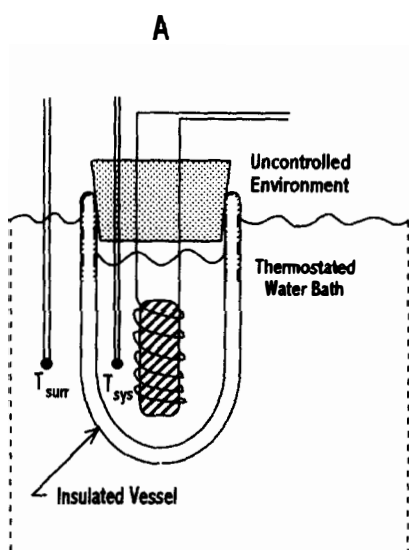
Schematic of Typical "Cold Fusion" Calorimeter

B
Thermopile
Metal Vessels
Reference   Sample
Thermostated Calorimetric Block

Schematic of Typical Commercially Available Heat-Conduction Calorimeter

Fig. 1. A comparison of typical heat-conduction calorimeter designs used in 'cold fusion' studies and in proven, commercially available instruments.

In 'cold fusion' type calorimeters (Fig. 1A), on which most claims of 'excess heat' [9–14] are based, several complications are immediately apparent. An evacuated Dewar flask or similar insulated vessel provides a low thermal conductivity from the reaction vessel to the environment and, thereby, increases the sensitivity by decreasing G. However, the time constant, τ, is proportional to G^{-1}, and thus a vessel with a small value of G must take a very long time to reach the steady state, thus, invalidating Eq. (2) under most conditions [5]. Events occurring in less than 6τ must be evaluated with help of Eq. (1), and not Eq. (2). Part of the proper calibration procedure is to verify that the calorimeter obeys Eqs. (1) and (2) under the conditions it will be operated. Furthermore, Eq. (1) does not apply to systems with multiple, disparate time constants. For example, a Dewar flask [14] or thickly insulated vessel [12] has a time constant associated with each thermal path to the surroundings, e.g. through the top, through electrical leads, through the glass, through the silver on the glass, and through radiation, that differ significantly, but all apply to thermal paths that make a significant contribution to heat exchange with the surroundings. For example, heat transfer by radiation and conduction can be comparable, but have different time constants in the Dewar flasks. Fleischmann et al. [14] neglected conductive heat transfer and assumed only radiative heat transfer in their data analysis, but calculations (Table 1) demonstrate that conduction of heat through the glass and the silver can be significant.

The typical design shown in Fig. 1A also raises the following question: Are the effective thermal conductivities of all heat transfer paths to the environment constant? Because the thermal conductivity through the vessel walls is so much smaller than through the electrical leads, etc., that go through the top, heat exchange with the surroundings through the lid may be significant compared with, or even greater than, the heat exchange with the bath through the walls.

In calorimeters similar to the design in Fig. 1A, another untested assumption is that the calorimeter and surrounding temperatures are accurately represented by the temperatures measured at single points in each. Any thermal gradients present in the solution or the surroundings could greatly influence the results. This systematic error may also be the basis for claims of 'excess heat' in flow calorimeters such as those of McKubre [15] and Patterson (as described in [16,17]). Heat-rate measurement in these flow calorimeters also depends on measurement of θ, the accuracy of which could easily suffer from the presence of temperature gradients and unaccounted-for thermal paths to the surroundings. Such isoperibol, temperature-rise, flow

Table 1

Relative importance of heat transfer by conductance and radiation in evacuated Dewar flasks

Glass thickness/ cm	Silver thickness/ cm	Glass, heat rate by conduction [a]/ mW	Silver, heat rate by conduction [a]/ mW	Glass, heat rate by radiation [b]/ mW	Ratio of heat rate by conduction to heat rate by radiation [c]/ %
Assumptions: (1) Dewar has 10 cm circumference; (2) Height of unsilvered glass is 8 cm; (3) ΔT of 1 K at 300 K; and (4) 5 cm from solution to top of Dewar. See Fig. 1A.					
0.1	0.001	2.343	8.54	50.36	22
0.01	0.0001	0.2343	0.854	50.36	2
0.1	0.0001	2.343	0.854	50.36	6
0.01	0.001	0.2343	8.54	50.36	17
Assumptions: (1) Dewar has 10 cm circumference; (2) Height of unsilvered glass is 4 cm; (3) ΔT of 1 K at 300 K; and (4) 3 cm from solution to top of Dewar.					
0.1	0.001	3.905	14.23	27.47	66
0.01	0.0001	0.3905	1.423	27.47	7
0.1	0.0001	3.905	1.423	27.47	19
0.01	0.001	0.3905	14.23	27.47	53

[a] Calculated with heat rate $= \lambda(\text{area})(\Delta T)/(\text{length})$, where area = circumference × thickness of material and λ is the thermal conductivity.
[b] Calculated with Stefan's law, heat rate $= R(\text{area}) = e\sigma(T_1^4 - T_2^4)(\text{area})$, where area = unsilvered area of Dewar.
[c] Sum of conduction heat rates for glass and silver layers, radiation from unsilvered glass only because heat rate from silvered glass is only 2% of unsilvered.

calorimeters have not proven to be generally useful because of such problems [18].

A minimum requirement to establish the accuracy of a calorimeter is verification of electrical calibration with a known chemical reaction [19], a requirement 'cold fusion' workers have largely chosen to ignore. In heat-conduction calorimeters with single-point temperature measurement, it is also necessary to show that the calibration constant is independent of the location of the calibration heater and temperature sensors in the vessel [20]. With the 'cold fusion' type heat-conduction calorimeter constructed in this study, when stirring was inadequate, we were able to repeatedly produce apparent 'excess heat' (either positive or negative) with a known chemical reaction, simply by changing the position of the heater or temperature sensors. Because the type of calorimeter illustrated in Fig. 1A has many potential applications other than 'cold fusion', this study defines the conditions under which accurate results can be obtained.

2. The calorimeter

The isoperibol, heat-conduction calorimeter (Fig. 2) was built from a brass tube, 38 mm (1.5 inch)

i.d. and 178 mm long, with brass plates soldered on both ends. The top plate has 16 tubes of 6.35 mm (0.25 inch) i.d. soldered into holes around the perimeter, and one large hole in the center for the reaction vessel. Seven of the holes in the top are inlets from the constant temperature bath and discharge at the bottom of the jacket while seven others are outlet tubes, alternately placed between the inlets, to carry water off the top of the jacket. (Because of the appearance of the 14 curved tubes coming out of the top in a symmetrical pattern, the instrument has been nick-named the *Octopus*.) The remaining two openings have tubes sealed and soldered at the bottom to serve as wells for thermocouples and thermistors which measure the jacket temperature. The wells are filled with water to improve thermal conductivity. Water is circulated through the jacket at $> 5\,l\,min^{-1}$ from the constant temperature bath (Hart Scientific Model 5024) that maintains temperature within ± 0.2 mK. The bath was set at 25.2°C. The bath could more easily serve as the outer jacket, but this particular calorimeter was designed to be operated in a location remote from the bath.

The reaction vessel is a 135 mm × 20 mm Pyrex test tube glued to a threaded brass head that screws into the brass jacket (Fig. 3). A Teflon bearing is fitted in the
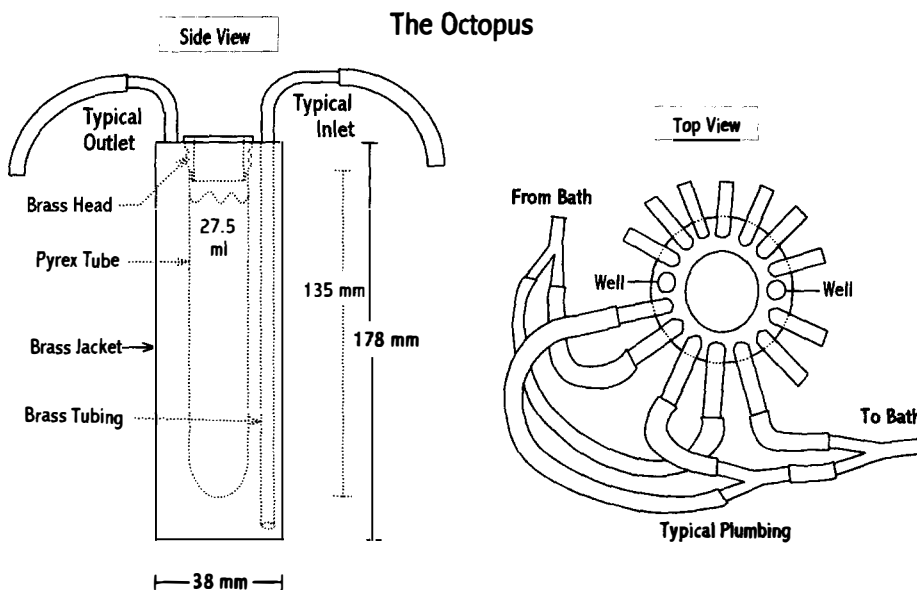

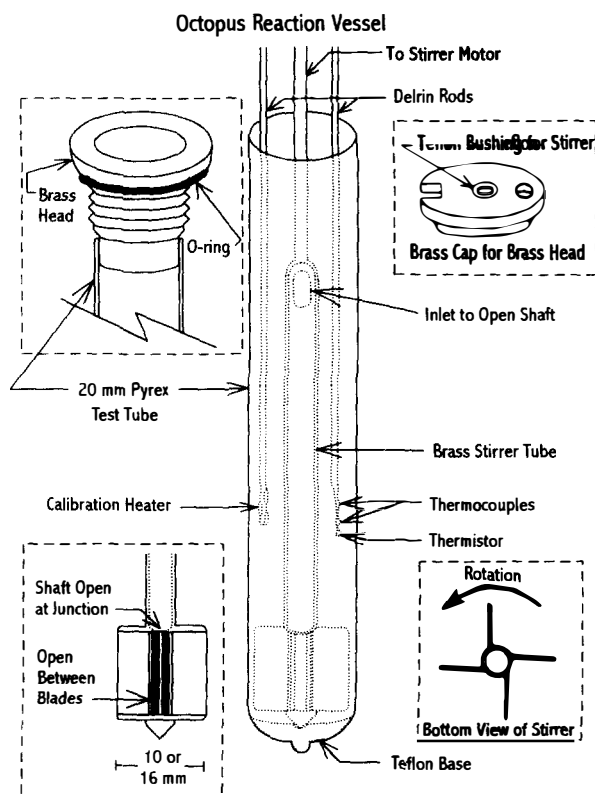Fig. 2. Octopus calorimeter – design and dimensions.

Fig. 3. Octopus reaction vessel details.

bottom of the test tube to stabilize the stirrer. The vessel holds 27.5 ml of solution. The stirrer (epoxy coated brass) is driven by a 1000 rpm synchronous motor. The brass cap contains a Teflon bushing in the center through which the stirring rod extends, two stationary Delrin rods (≈2 mm o.d.) that extend down into the cell, and two holes to allow for escaping gas and for adding or removing liquids. The calibration heater (37.2 Ω total) is constructed of three wire-wound resistors in series to increase surface area and heat transfer to the solution. The heater leads are 32 gage Cu ca. 50 cm long. Four leads were used, two for current conduction and two to measure the voltage at the resistors. The heater and a 1 mm o.d. Teflon tube for liquid addition are attached to one of the Delrin rods. The end of the Teflon tube is in the middle of the calibration heater. The voltage for the calibration heater is supplied by a control panel from a Tronac Model 450 calorimeter. The wire-wound resistor (2.051 Ω) used to determine heater current

was calibrated against 1, 10 and 100 Ω standard resistors.

The other Delrin rod supports two thermocouples and a thermistor. The temperature sensors were first coated with epoxy, then placed in Teflon heat-shrink tubing and the ends sealed with silicone rubber. The sensors were attached to the rod to prevent lateral or vertical movement. The thermocouples (copper–Constantan) provide redundant confirmation of the thermistor response and, though not as sensitive to ΔT as thermistors, thermocouples are not susceptible to errors caused by self-heating. The thermistors are glass encapsulated 10 kΩ with a 10 V power supply across the bridge. Inside the vessel, wiring for the heater, thermistor and thermocouples was encapsulated in heat-shrink Teflon tubing. To avoid unwanted Seebeck effects in the temperature sensor circuits, connections were made on a terminal block fastened to an aluminum block (112 × 112 × 13 mm^3) attached at the top of the jacket.

To eliminate the possibility of systematic errors in the ΔT measurement, the calorimeter vessel has three temperature sensors, one thermistor and two thermocouples. The differential thermistor bridge (≈0.1 V K^{-1}) measures the ΔT between the vessel and a well in the jacket (Figs. 2 and 3). One thermocouple pair (≈40 μV K^{-1}) measures ΔT between the vessel and the other well of the jacket in a similar way. The second thermocouple pair measures ΔT between the cell and an exterior ice bath. If the calorimeter is working properly all three sensors should record equivalent responses to a heat effect.

Data collection is done through an IEEE board attached to a Keithley Model 195 digital multimeter and a Hewlett–Packard 3488A multiplexer (Fig. 4). Data collected during an experiment typically include elapsed time interval, heater voltage, heater current (voltage across a calibrated resistor), thermocouple voltage 1 (vessel and jacket), thermocouple voltage 2 (vessel and ice bath) and thermistor–bridge–unbalance voltage (vessel and jacket). Data are typically collected every 22 s.

The shape of the reaction vessel (a tall, narrow test tube) made mixing in the vertical direction difficult, so the stirrer was designed to pump solution downward through the tubular shaft. Four blades at the base of the open shaft create a reduced pressure at the junction of the shaft with the blades (Fig. 3). Mixing was tested
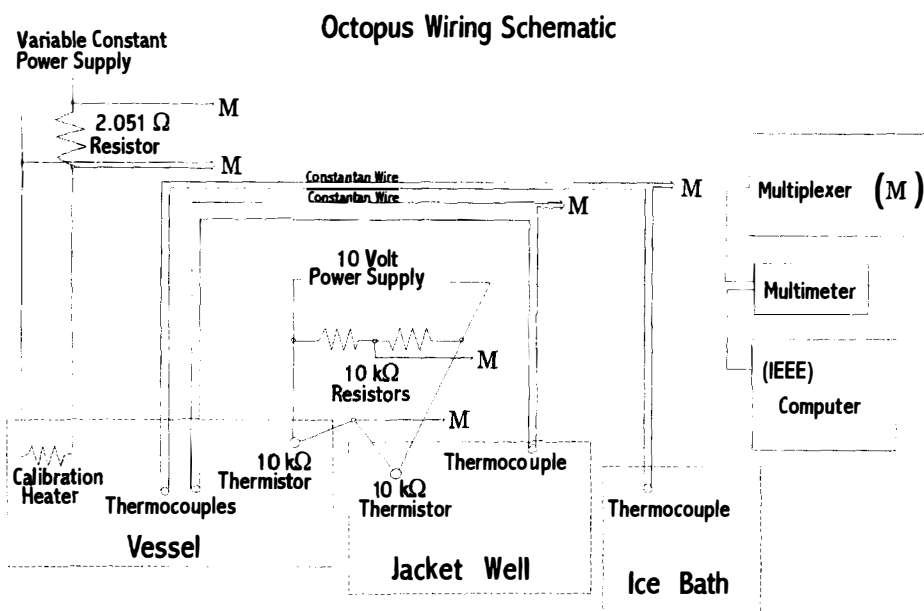
Octopus Wiring Schematic

Fig. 4. Octopus wiring schematic.

by observing the mixing of dye injections. Visually, stirring appeared to be very rapid, at 1000 rpm ($<$ 1 s).

The heat of dilution of 1-propanol was used as one standard test reaction to verify the electrical calibration. The amount of heat generated (176 $\pm$ 3 J), when 1.02 ml (4 min injection at 255 $\pm$ 1 μl min^{-1} from a motorized buret) of neat 1-propanol was added to 27 ml of a 0.030 M solution, was first determined on a Tronac model 450 titration calorimeter. Total heat at intermediate points was also determined, and the heat generated was linear with quantity added, the intercept being equal to zero within the limits of error. A second standard test reaction, addition of perchloric acid solution (4.42 M) to Tris (tris[hydroxymethyl]a-minomethane) base solution (0.25 M prepared by weight) was used to confirm the 1-propanol dilution results. The enthalpy change of the reaction determined with a Tronac Model 450 titration calorimeter (47.24 kJ mol^{-1}) was within the limits of error of the literature [21] value (47.36 $\pm$ 0.25 kJ mol^{-1}).

3. Results and discussion

Table 2A gives the baseline noise and temperature detection limits for the temperature sensors with the

Table 2
Baseline noise and detection limit

	Standard deviation of the baseline [a] / μV	Detection limit [b], ΔT / K
A. Original stirrer		
thermistor	94	0.0028
thermocouple vs. bath	0.71	0.053
thermocouple vs. ice	1.0	0.075
B. Improved stirrer		
thermistor	51	0.0015
thermocouple vs. bath	0.78	0.059
thermocouple vs. ice	0.66	0.049

[a] The noise level over a 6 h run.
[b] The detection limit is three times the standard deviation of the noise divided by the sensitivity.

first stirrer constructed. By switching the heater on or off, the calorimeter time constant (τ), defined by the equation $V = ae^{-(t/\tau)}$ (where V is the thermistor bridge unbalance voltage, a a constant and t the time), was determined to be $\approx$0.5 min by fitting the voltage–time curve. After the heat transfer rate stabilized with the heater on, the temperature rise was constant with less than 5% peak-to-peak noise.

The calibration constant was calculated in two different ways. First, G was calculated as the slope of the line in a plot of the change in voltage of the thermistor bridge against the heater power. The value of G' was calculated as the slope of the line in a plot of the area under the temperature–time curve against the total heat from the heater. Both plots were linear from 0.02 to 4 W (5 to 1200 J) with zero intercepts. Area was determined with the trapezoidal rule: $\int f(t)\mathrm{d}t \approx \sum 1/2[V_2 + V_1][t_2 - t_1]$. (To distinguish G from G', G values are given with units of W mV^{-1} and G' values are displayed with units of J s^{-1} mV^{-1}: note that J s^{-1} = W.) The value of G^{-1} was found to be 25.3 mV W^{-1}, and G'^{-1} – 25.1 mV s J^{-1}. Because the volume changes during the experiment, the calorimeter was calibrated at various liquid volumes. The response of the thermistor bridge (V) was plotted against the input wattage while the volume of water was changed from 25.5 ml to 28 ml. The calibration constant varied only slightly. The change in G is < 1.7 W mV^{-1} or ≈2% per ml change in volume (at 0.8 W of power).

Several tests were performed in which the calibration heater was on for a period, after which a four minute injection of 1-propanol was made, followed by turning on the calibration heater again (Fig. 5). The response of the thermistor bridge to the calibration heater was 8% greater than the response produced by the injection of 1-propanol (Table 3). It was apparent that large systematic errors were present. These results were further tested with the perchloric acid-Tris reaction. The acid-base reaction in the Octopus gave the
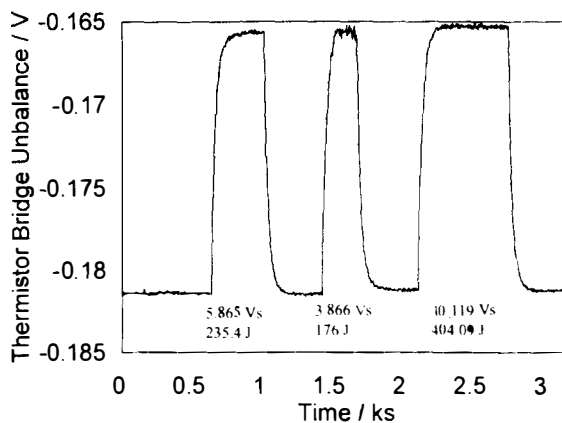

Fig. 5. Typical calibration data from the thermistor bridge (see D1, Table 3).

same 8% difference, indicating that the problem was not with the chemical reactions, but with the calorimeter.

Moving the calibration heater gave a different calibration constant at each new position. The results with position were random, i.e. the lowest position (one-third of the way up the vessel) gave a constant ca. 18% high, while the highest position (two-thirds of the way up the vessel) gave a constant in agreement with the chemical reaction heats, and an intermediate position (middle of the vessel) gave a constant ca. 18% low. We concluded that the point temperature sensors were not measuring the average solution temperature. This source of systematic error probably accounts for many of the reports of 'excess heat' and much of the

Table 3
Calorimetric constant determined with electrical heating compared to injection of 1-propanol (original stirrer)[a]. Note the 8% difference between results of electrical and chemical calibrations

Run	Heater energy/ J	Response/ V s	$[G']^{-1}/$ mV s J^{-1}	Injection energy/ J	Response/ V s[b]	$[G']^{-1}$ in V sJ^{-1}	Heater energy/ J	Response/ V s	$[G']^{-1}/$ mV s J^{-1}
A1	234.1	5.878	25.1	176	4.061	23.7	331.1	8.277	25.0
B1	607.4	15.21	25.0	176	3.929	22.9	952.1	24.06	25.3
C1	247.2	6.251	25.3	176	3.925	22.9	275.7	6.969	25.3
D1	235.4	5.865	24.9	176	3.866	22.6	404.1	10.12	25.0
E1	275.9	6.925	25.1	176	3.968	23.1	262.6	6.599	25.1
F1	193.7	4.893	25.3	176	4.096	23.9	249.9	6.320	25.3
G1	485.1	12.18	25.1	176	4.041	23.6	606.4	15.38	25.4
H1	1562	38.48	24.6	176	3.877	22.6	438.8	10.78	24.6
Average			25.1			23.2			25.1

[a] G^{-1} = 25.1 ± 0.3 mV s J^{-1} when determined with electrical heating and 23.2 ± 0.5 mV s J^{-1} with chemical injection. [b] Values adjusted for heat change due to the introduction of a liquid cooler than the calorimeter.

Table 4
Calorimetric constant determined with electrical heating compared to chemical reaction [a] (improved stirrer)

Run	Injection energy/ J [b]	Response/ V s	$[G]^{-1}/$ mV s J^{-1}	Heater energy/ J	Response/ V s	$[G']^{-1}/$ mV s J^{-1}
A2	176	4.37	25.6	189.6	4.75	25.1
B2	176	4.32	25.3	151.7	3.82	25.2
C2	176	4.37	25.6	151.7	3.82	25.2
D2	176	4.29	25.1	151.7	3.83	25.2
J2	176	4.31	25.2	151.7	3.82	25.2
K2	176	4.32	25.3	151.7	3.80	25.0
A3	215	5.24	25.0	151.6	3.78	24.9
B3	215	5.28	25.2	151.6	3.81	25.1
C3	215	5.17	24.7	151.6	3.75	24.7
D3	215	5.20	24.8	151.6	3.80	25.1
Average			25.2 ± 0.3			25.1 ± 0.2

[a] Runs A2-D2 and J2-K2 are 1-propanol dilution. Runs A3-D3 are perchloric acid-tris reactions.
[b] Values adjusted for heat change due to introduction of liquid cooler than the calorimeter.

irreproducibility of 'cold fusion' calorimetry. The percent 'excess heat', as also the production of any 'excess heat', is seldom a reproducible result in the 'cold fusion' articles reviewed [9–14]. Previous explanations for the irreproducibility usually focused on defects, 'contamination', or improper manufacture of the cathode, but deficiencies in calorimeter construction and calibration are a more probable explanation.

The influence of the stirrer was investigated by changing the stirrer motor from 1000 to 600 and 200 rpm. 'Excess heat' increased as the rpm was reduced, from ca. 8% at 1000 rpm to ca. 11% at 600 rpm to ca. 40% at 200 rpm. Despite visual indications, using dye injection, that stirring was adequate [11], these results show that it was not.

The stirrer was improved by reducing the shaft from 6.35 to 4.76 mm o.d. and increasing the impeller diameter from 10 to 16 mm. The new stirrer was operated only at 1000 rpm. Both chemical reactions were again used to test the calorimeter. The results are given in Table 2B and Table 4. A slight decrease in baseline noise was noted with the improved stirrer. Difference between response to the calibration heater and a chemical reaction was < 1% (Table 4). The calorimeter was retested at various liquid volumes. The response of the thermistors (V) was plotted against the input heat rate while the volume of liquid was changed from 26.5 to 29 ml. The change in G was again <2% per ml volume change (at 0.8 W of power).

4. Conclusion

Stability and repeatability are not sufficient verification of the accuracy of a calorimeter. A chemical reaction with a known heat effect should always be used to verify electrical calibration. The accuracy of heat-conduction calorimeters with point temperature sensors can be significantly affected by inadequate mixing. The time constant of mixing must be much smaller than the time constant of heat transfer to the surroundings, otherwise the rate of heat transfer measured by point sensors will depend on the location of the heat source. Even when mixing appears to be rapid, electrical heating can produce calibration constants with large errors. Up to a 40% different response (i.e. 'excess heat') between the heater and a chemical reaction was observed in this study. If the calorimeter is designed properly and mixing speed is adequate, location of point temperature sensors in the vessel will not affect the results. The lack of reproducibility in 'cold fusion' experiments is the expected and observed result from systematic errors arising from use of single-point temperature sensing in a heat-conduction type of calorimeter.

Problems in 'cold fusion' calorimeters include inadequate stirring, unstable heat paths, and inadequate calibration to validate use of point temperature sensors. Claims of 'excess heat' based on measurements with the type of calorimeter illustrated in Fig. 1A should not be accepted until all these problems have been resolved. Observations of 'excess

heat' are more likely due to calorimetric errors than to violations of the laws of thermodynamics, or to known or unknown nuclear or chemical reactions.

Acknowledgements

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