Research Article

# The Fleischmann–Pons Calorimetric Methods, Equations and New Applications

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**Abstract**

The Fleischmann–Pons Dewar isoperibolic calorimetry remains the most accurate system for measuring excess power in cold fusion experiments. The use of mathematical modelling and numerical integration of the experiment data, along with appropriate averaging methods, can achieve a calorimetric accuracy of $\pm 0.1$ mW. The Fleischmann–Pons "Lower Bound Method" can be used to determine the heat-transfer co-efficient during an experiment and yields accurate results. Important information can be obtained from time periods where the cell is first turned on and when the cell is shut off. Periods of large cell temperature changes are accurately modelled by the differential equations. These Fleischmann–Pons calorimetric methods and equations are applied to a new experiment where excess power is produced in the Pd/$D_2O$ + 0.1 M $KNO_3$ systems. A heat conduction calorimeter was used in this study, but the same methods and equations apply.
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*Keywords:* Cell cooling, Cell heating, Deuterium oxide, Differential equations, Excess power, Lower bound method, Palladium

**Remarks from Dr. Jean-Paul Biberian (Editor-in-Chief)**

This paper by Melvin Miles is an important contribution to the understanding of the calorimetry developed by Martin Fleischmann and Stanley Pons in their original work. As in many major discoveries, an inventor creates his own instrument. Fleischmann and Pons built a new type of very simple and accurate calorimeter with unusually high precision. The quality of their apparatus allowed them to make their discovery. Both in the past and present their method has been challenged. It is the purpose of this paper to give a clear view of this unique device. As I do for all papers published in the journal, I have asked a first referee to analyze the paper. As the reviewer raised a number of questions, I asked the advice of a second reviewer. In the end, I decided to publish the paper together with the comments of the reviewers and the answers of the author. This is unusual, but not unprecedented. This way of doing things has the advantage for the reader, who will have in hand all the pros and cons to make his own evaluation of the work (see the Comments of Referees at the end of this article).

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## 1. Introduction

Martin Fleischmann had remarkable skills in mathematical modelling and had made many notable contributions to science prior to the Fleischmann–Pons discovery of cold fusion [1]. Stanley Pons was also recognized as a top electrochemist with considerable computer skills. Together they developed the accurate Fleischmann–Pons Dewar isoperibolic calorimetry with computerized data acquisition [2–4]. However, the vastly inferior calorimetric experiments by CalTech, MIT and Harwell, along with personal ridicule, blocked the scientific acceptance of cold fusion in 1989 [5]. An important new scientific discovery soon became a scientific tragedy. Many cold fusion scientists who had observed cold fusion effects in their experiments and continued this research suffered severe career damage. This stigmatizing of cold fusion research for the past 28 years is the real scientific fiasco. Fleischmann and Pons were correct. Sometimes scientists get it wrong, but important discoveries have often been rejected for many years (Galileo, Joule, Semmelweis, Arrhenius, Wegener and many others).

There are numerous reasons why this Fleischmann–Pons calorimetry is still important today – nearly 28 years later. The accuracy of the Fleischmann–Pons calorimetry was the major topic of the 1989 cold fusion controversy, and the field has never recovered from the CalTech, MIT and Harwell rejections of this calorimetry. This mathematically based calorimetry remains poorly understood by most scientists, and this includes many cold fusion researchers. This calorimetry continues as the most accurate for electrochemical reactions and has a very small error of only $\pm$ 0.1 mW when correctly applied [6]. This calorimetry also has possible applications for many other electrochemical studies in addition to cold fusion.

The advantages of the Fleischmann–Pons Dewar cell are that: (1) it provides a direct view inside the cell during an experiment, (2) it has no memory effect because of the direct heat transfer by radiation photons, (3) the Stefan–Boltzmann constant ($5.670373 \times 10^{-8}$ $Wm^{-2}K^{-4}$) along with the cell surface area provides an estimate of the radiative heat transfer co-efficient, (4) it provides a wide dynamic range for the cell temperature (100 K) and cell voltage (10 V), (5) the small cell diameter (2.5 cm) provides good mixing by the electrolysis gases, (6) the inherent safety and self-purifying effects provided by the gases exiting the cell, and (7) the high accuracy achieved by computer data acquisition and mathematical modelling.

These cold fusion calorimetric experiments consist of four measurements: the cell temperature, the bath temperature, the cell current, and the cell voltage. The temperature measurements are the least accurate. Because of this, Fleischmann and Pons measured temperatures to within $\pm0.001$ K by using calibrated thermistors. In contrast, CalTech measured temperatures to within $\pm0.03$ K while MIT and Harwell measured temperatures to only within $\pm0.1$ K. For a typical difference of 10.0 K between the cell and bath temperature and a 1.0 W cell input power, the minimum possible error would be $\pm0.1$ mW for the Fleischmann–Pons calorimetry, $\pm3$ mW for the CalTech calorimetry, and $\pm10$ mW for the MIT and Harwell calorimetry. The averaging of data and the use of mathematical modelling allowed Fleischmann and Pons to reach their limit of $\pm$ 0.1 mW while the MIT calorimetric error was reported as $\pm50$ mW [7].

## 2. Experimental

A new experiment was designed to test some of the Fleischmann–Pons calorimetric methods and equations. However, this experiment was done in a copper calorimeter with heat transfer by conduction [8]. Furthermore, the electrolyte of $KNO_3$ was lithium-free to test proposals of lithium being involved in the production of excess heat [9]. Nevertheless, the same equations and methods, as used by Fleischmann–Pons calorimetry, were applied.

The palladium wire cathode (1.0 mm × 23 mm) was from a Johnson–Matthey) source that had previously provided cathodes which produced excess heat at China Lake as well as at NHE in Japan [10,11]. This $Pd/D_2O + 0.1$ M $KNO_3$ cell was prepared using Cambridge Isotope Laboratories $D_2O$ (99.9 atom% D). Previous control experiments produced no excess heat with $Pd/H_2O + 0.1$ M $KNO_3$ using this calorimeter [8].

This calorimetric experiment involved two thermistors fixed in position on opposite sides of the cell wall and immersed in a heat transfer fluid (Mobil-1 oil) as reported previously [8,12,13]. The cell and thermistors fit tightly into the inner calorimetric chamber. This cell was equipped with a centering ring at the cell top which prevented any shift in the cell position. This same calorimeter was used in co-deposition studies of palladium, ruthenium and other transition metals [12,13].

The results for this experiment are based on one thermistors used for the cell ($T_2$) and one used for the bath ($T_3$). These two thermistors always showed excellent stability ($\pm 0.005$ K) and passed all calibration tests both before and following this experiment. A third thermistor ($T_5$) on the opposite side of the cell wall occasionally showed erratic behavior and failed calibration tests following this experiment. However, there were periods where both thermistor gave good agreement as found in previous experiments [8,12,13].

## 3. Lower Bound Method

This method assumes that the excess power is zero and then calculates the lower bound heat transfer co-efficient ($k'$) resulting from this assumption [3]. The calorimetric equations based on the First Law of Thermodynamics expressed as power is

$$C_{\mathrm{p}} M \, \mathrm{d}T/\mathrm{d}t = P_{\mathrm{EI}} + P_{\mathrm{H}} + P_{\mathrm{X}} + P_{\mathrm{R}} + P_{\mathrm{C}} + P_{\mathrm{gas}} + P_{\mathrm{W}}. \tag{1}$$

This differential equation is always applied in the Fleischmann–Pons calorimetry. Positive power terms involving energy supplied to the cell are the electrochemical power ($P_{\mathrm{EI}}$), internal heater power ($P_{\mathrm{H}}$), if used, and any form of excess power ($P_{\mathrm{X}}$). The negative power terms for energy escaping the cell are heat radiation ($P_{\mathrm{R}}$), heat conduction ($P_{\mathrm{C}}$), heated gases ($P_{\mathrm{gas}}$), and the pressure–volume work done by the generated gases on the surroundings ($P_{\mathrm{W}}$). As a first approximation, the small $P_{\mathrm{gas}}$ and $P_{\mathrm{W}}$ terms can often be neglected. The first term involves the heat capacity of the calorimeter (JK$^{-1}$) expressed in terms of equivalent moles of $D_2O$ (M) and the molar heat capacity ($C_{\mathrm{p}}$) of $D_2O$ (84.35 J mol$^{-1}$K$^{-1}$). The rate of change of the cell temperature ($\mathrm{d}T/\mathrm{d}t$) depends on the relative rates of energy added to the cell and leaving the cell. However, $\mathrm{d}T/\mathrm{d}t$ is never exactly zero (no steady state) because of the changing electrolyte level in an open cell resulting in a changing heat transfer co-efficient [14]. Mathematical equations for these various power terms are given in Appendix A.

For heat conduction calorimetry, Eq. (1) can be expressed as

$$C_{\mathrm{p}} M \mathrm{d}T/\mathrm{d}t = P_{\mathrm{EI}} + P_{\mathrm{H}} + P_{\mathrm{X}} - k\,(T - T_{\mathrm{b}}) + P_{\mathrm{R}} + P_{\mathrm{g}} + P_{\mathrm{W}}. \tag{2}$$

Using the lower bound assumption of $P_{\mathrm{X}} = 0$ yields

$$C_{\mathrm{p}} M \, \mathrm{d}T/\mathrm{d}t = P_{\mathrm{EI}} + P_{\mathrm{H}} + 0 - k'(T - T_{\mathrm{b}}) + P_{\mathrm{R}} + P_{\mathrm{g}} + P_{\mathrm{W}}, \tag{3}$$

where $k'$ is the resulting lower bound cell constant. Equation (2) minus Eq. (3) yields

$$P_{\mathrm{X}} = (k - k')(T - T_{\mathrm{b}}). \tag{4}$$

Note that the lower bound $k'$ will always be less than or equal to the true heat transfer co-efficient, $k$. Because $P_{\mathrm{X}}$ will likely approach zero sometime during an experiment, the highest value obtained for $k'$ can be used to approximate the true $k$. If the true heat transfer co-efficient is known, then Eq. (4) provides a simple method for accurately calculating excess power. The lower bound heat transfer co-efficient can be calculated for each experimental point using

$$k' = (P_{\mathrm{EI}} + P_{\mathrm{H}} + P_{\mathrm{C}} + P_{\mathrm{g}} + P_{\mathrm{w}} - C_{\mathrm{p}} M \, \mathrm{d}T/\mathrm{d}t)/(T - T_{\mathrm{b}}), \tag{5}$$

where $P_C \gg P_R$ for a heat conduction calorimeter.

Rearranging Eq. (4) gives

$$k_C' = k_C - P_X/(T - T_b). \tag{6}$$

For Pd/$D_2$O or Pd/$H_2$O, the exothermic loading of palladium with deuterium or hydrogen will generally result in a small initial excess power effect. Therefore, $k'$ can be near zero or even negative initially when $T - T_b$ is very small [3]. Later, as $T - T_b$ increases and as the exothermic loading is completed, then $k'$ may approach $k$ in value. Equation (6) is similar to the equation $y = a - b/x$ as $x$ ranges from small to large values.

Initial experimental results for the lower bound constant, $k'$, versus time, are shown in Fig. 1 for the new Pd/$D_2$O + 0.1 M $KNO_3$ experiment. The value for $k'$ is near zero at 2 min and approaches the true $k = 0.1350$ W/K as the time increases. Previous control experiments using this same calorimeter have always given cell constants ranging from 0.1324 to 0.1340 W/K [8,12,13]. From the initial values for $k'$, it can be estimated that the excess power due to loading was about 5 mW. A sharp increase in $k'$ was noted near 50 min where the loading reaches about $x = 0.6$ for PdD$_X$ and the rate of deuterium loading decreases significantly. The results shown in Fig. 1 indicate that this palladium cathode loaded readily with deuterium. Also, there was an early excess power effect in addition to the exothermic loading of deuterium into the palladium which causes changes in $k'$ as shown in Fig. 1.

Equations derived by Fleischmann [14] show that the cell temperature measured inside the cell should initially increase linearly with time. This was approximately the behavior in this new Pd/$D_2$O + 0.1 M $KNO_3$ experiment where $dT/dt = 1.53 \times 10^{-4}$ K/s over the first 40 min. However, the cell temperature in this experiment was measured on the outside cell surface in a secondary compartment containing a heat transfer fluid (Mobil-1 oil) as in previous experiments [8,12,13]. This gave an episode from 6 to 12 min of nonlinear temperature changes due to the sluggish mixing of this fluid by convection. The theoretical cell heating rate is given by the Fleischmann–Pons equation
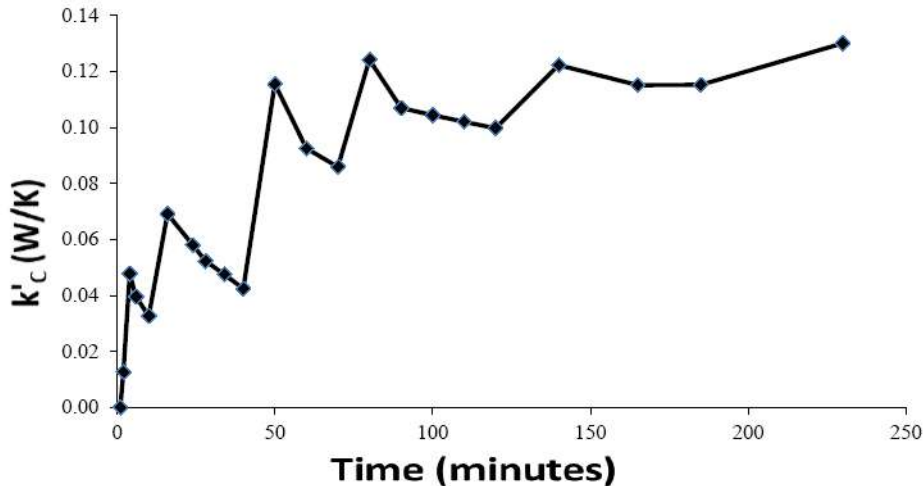
$$dT/dt = [(E - E_H)I + P_X - k(T - T_b)]/C_p M, \tag{7}$$



**Figure 1.** The lower bound cell constant versus time for the first 240 h ($I = 0.0365$ A).

where $C_pM = 450$ JK$^{-1}$, $k = 0.1350$ WK$^{-1}$ and $P_g$ and $P_W$ are small and can be neglected due to the initial low cell current ($I = 0.0365$ A). Table 1 gives the theoretical $dT/dt$ values for selected experimental measurements using Eq. (7).

The theoretical cell heating rate ($dT/dt$ calculated using Eq. (7) is nearly constant over the first 40 min with a mean value of $dT/dt = 1.59 \pm 0.04 \times 10^{-4}$ K s$^{-1}$. This is in good agreement with the mean experimental rate of $1.53 \times 10^{-4}$ K s$^{-1}$ and supports the $C_pM$ and $k$ values used as well as the measured excess power. The increases in excess power apparently extends the linear $dT/dt$ region for a longer time period than the expected 15–20 min [14]. The experimental rate of the cell heating between 45 and 65 min was measured as $0.83 \times 10^{-4}$ K s$^{-1}$ and again this is in good agreement with the theoretical rates at 50 and 60 min shown in Table 1. The agreement between the theoretical and experimental values for $dT/dt$ shows that Eq. (7) provides a good mathematical model for the cell behavior.

## 4. Excess Power Measurements

The excess power for this Pd/D$_2$O + 0.1 M KNO$_3$ experiment is shown in Fig. 2. These values for excess power were calculated using the Lower Bound Method as expressed by Eqs. (4) and (5). The mean excess power value for each day is displayed or split excess powers on days when the current is changed. An excess power effect in addition to the 5 mW exothermic deuterium loading was observed for the first day of this experiment as shown in Table 1. Larger excess power effects were observed when the cell current increases from 36.5 to 146 mA on Day 4, to 219 mA on Day 7, and to 292 mA on Day 8. The additions of make-up D$_2$O caused the excess power to decrease (5.2 mL on Day 6, 6.6 mL on Day 8, and 5.2 mL on Day 12). This decreases in the excess power is generally explained by the resulting cell cooling or by the introduction of H$_2$O contamination. The largest excess power was 73 mW on Day 8 at a cell current of 292 mA (0.400 A cm$^{-2}$). This yields 3.65 W/cm$^3$ for this small palladium cathode ($0.1 \times 2.3$ cm, $V = 0.020$ cm$^3$). This is the normally expected value of 1–5 W/cm$^3$ for these electrolysis experiments [5].

These excess power calculations used $k = 0.1350$ W K$^{-1}$ for a cell filled with 50 mL of D$_2$O giving $C_pM = 450$ J K$^{-1}$. The changes in the cell electrolyte volume were calculated by Faraday's law (–0.812 mL of D$_2$O per day at a cell current of 100 mA). From previous experiments, the cell constant varies by 0.0002 W K$^{-1}$ per mL, and the heat capacity changes by 4.65 JK$^{-1}$ per mL of D$_2$O [12,13]. These changes were applied each day in the calculations of the excess power.

There is a good explanation for the zero excess power results for Day 13. At the end of Day 12, the cell was turned off to obtain results for the rate of the cell cooling. This cell cooling was measured with the cell turned off for 133 min allowing the deuterium inside the palladium to escape (deload). Furthermore, 5.2 mL of D$_2$O was then added followed by turning the cell back on at a higher current of 365 mA (500 mA/cm$^2$). The next day (Day 13), the mean excess power was –23.0 mW. However, the $P_g$ and $P_W$ terms had been neglected for simplicity. Because of the high cell current and high cell temperature (about 43°C), it was calculated that $P_g = -16.2$ mW and $P_W = -7.5$ mW. Adding these two neglected terms gave a mean excess power of 0.7 mW for Day 13. Because of this result, the mean

**Table 1.** Theoretical cell heating rates ($dT/dt$).

| Time (min) | $E$ (V)[a] | $P_X$ (W) | $dT/dt$ (K s$^{-1}$) |
|---|---|---|---|
| 10 | 3.625 | 0.0235 | $1.61 \times 10^{-4}$ |
| 20 | 3.850 | 0.0163 | $1.55 \times 10^{-4}$ |
| 30 | 3.899 | 0.0290 | $1.62 \times 10^{-4}$ |
| 40 | 3.922 | 0.0380 | $1.55 \times 10^{-4}$ |
| 50 | 3.944 | 0.0094 | $0.73 \times 10^{-4}$ |
| 60 | 3.956 | 0.0229 | $0.86 \times 10^{-4}$ |

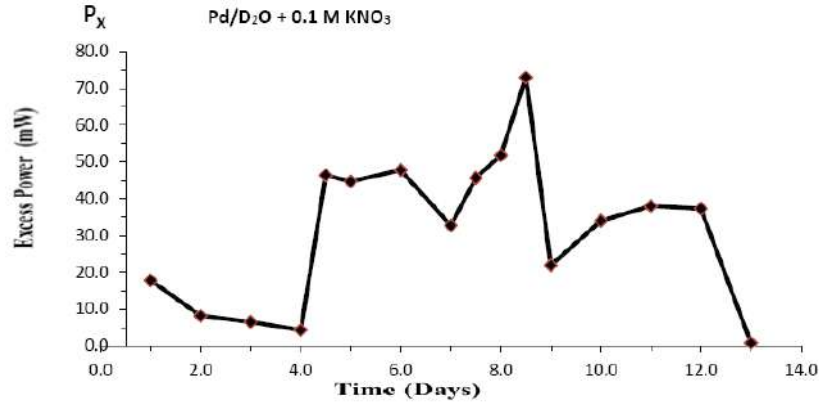[a] Cell current ($I$) was 0.0365 A.

**Figure 2.** Mean values for the excess power measurements for each time period.

$P_X$ values for all other days were corrected for the small $P_g + P_W$ sum on each day. These results for Day 13 indicate the accurate modelling of this calorimeter and show the importance of not neglecting the $P_g$ and $P_W$ terms when the excess power is close to zero.

## 5. Cell Cooling Study

For cell cooling with $I = 0$, most calorimetric terms are zero, leaving the simple differential equation (assuming $P_X = 0$)

$$C_p M \, \mathrm{d}T/\mathrm{d}t = -k(T - T_b). \tag{8}$$

This equation is readily integrated to give

$$\ln(T_o - T_b)/(T - T_b) = (k/C_p M)t. \tag{9}$$

This integrated equation can also be written as

$$\Delta T = \Delta T_o \, \exp(-kt/C_p M), \tag{10}$$

where $\Delta T = T - T_b$ and $\Delta T_o = T_o - T_b$. Related equations for radiative heat transfer during the cell cooling, as in the Fleischmann–Pons Dewar cell, are given in Appendix B. The cooling curve equations are actually quite similar for conductive and radiative heat transfer with only additional small terms for radiative cooling (see Eq. (B.2)).

The expected exponential decreases in $\Delta T$ is shown in Fig. 3 for this Pd/D$_2$O + 0.1 M KNO$_3$ experiment. Initially, the decrease in the cell temperature is almost linear with time as shown both in Figs. 3 and 4. Except for the first two points in Fig. 4, there is almost a linear decrease in $\Delta T$ from 2 to 14 min. This is explained by Eq. (10) for small values for time ($t$) where

$$\Delta T = \Delta T_o(l - -kt/C_p M). \tag{11}$$

The theoretical cell cooling rate can also be expressed by the differential equation

$$\mathrm{d}T/\mathrm{d}t = (-k\Delta T + P_X - P_X')/C_p M, \tag{12}$$

where $P_X$ is any lingering excess power when the cell is off and $P_X'$ represents the endothermic deloading of deuterium from the palladium. This deloading will be very fast when the cell is first turned off. Any excess power
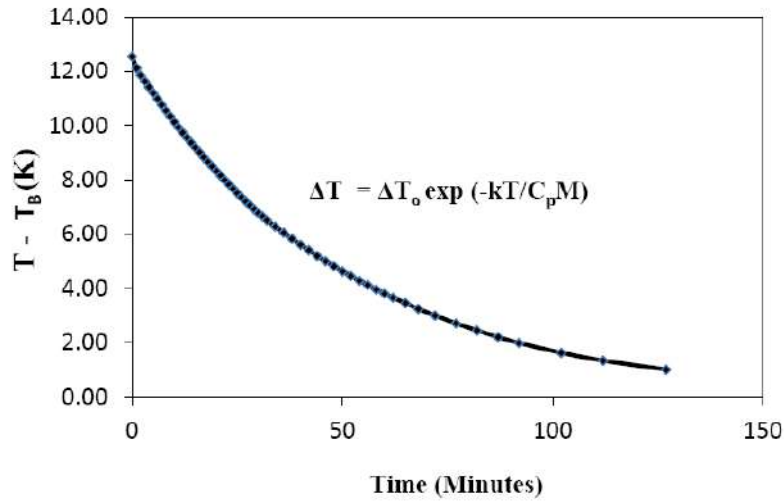
**Figure 3.** Experimental cell cooling at zero current for 130 min.

(heat-after-death) will slow down the cell cooling rate while the endothermic deloading will increase the cell cooling rate. However, $P_X$ and $P'_X$ are unknown, and we can only look for any possible effects that they may exert on the experimental cooling rates. Assuming $P_X - P'_X = 0$, the experimental and theoretical cooling rates are compared in Table 2. Due to the low level of $D_2O$ during this cell cooling experiment (44 mL), $k = 0.1338 \, \mathrm{WK}^{-1}$ and $C_pM = 410 \, \mathrm{JK}^{-1}$.

The initial high experimental rate of cell cooling could be explained by the rapid deloading of deuterium. Oth-
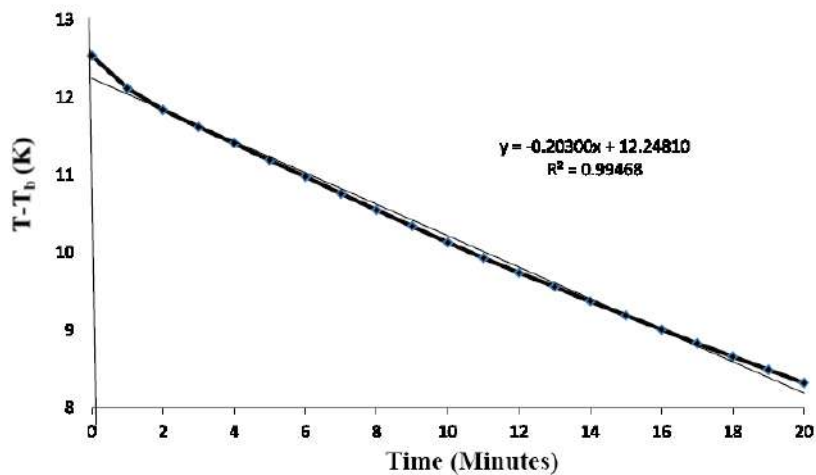


**Figure 4.** Initial cell cooling for the first 20 min.

**Table 2.** Experimental versus theoretical cooling rates for the Pd/$D_2O$ + 0.1 M $KNO_3$ cell.

| Time (min) | $\Delta T$ (K) | Experimental (K/min) | Theoretical (K/min)[a] |
|---|---|---|---|
| 2 | 11.84 | –0.28 | –0.232 |
| 5 | 11.19 | –0.22 | –0.219 |
| 10 | 10.31 | –0.21 | –0.202 |
| 15 | 9.19 | –0.18 | –0.180 |
| 20 | 8.32 | –0.17 | –0.163 |
| 30 | 6.77 | –0.14 | –0.133 |
| 40 | 5.61 | –0.11 | –0.110 |
| 50 | 4.63 | –0.09 | –0.091 |

[a] From Eq. (12) with $P_X - P'_X = 0$, $k = 0.1338$ WK$^{-1}$, and $C_pM = 410$ JK$^{-1}$.

erwise, the experimental and theoretical cell cooling rates are in good agreement. If the excess power of 0.038 W continued with the cell off, this would only slow the cooling rate by 0.038 W/410 JK$^{-1} = 9.3 \times 10^{-5}$ K/s or by 0.0056 K/min and would be difficult to detect.

The cell cooling expressed by the integrated equation (Eq. (9)) is shown in Fig. 5. An excellent fit ($R^2 = 0.9999$) to the straight-line behavior is observed with the line slope equal to 0.01974 min$^{-1}$ or $3.290 \times 10^{-4}$ s$^{-1}$. This agrees reasonably well with the expected slope of $3.2963 \times 10^{-4}$ s$^{-1}$ given by $k/C_pM$ where $k = 0.1338$ WK$^{-1}$ and $C_pM = 410$ JK$^{-1}$. Fleischmann and Pons have reported large deviations from the expected straight-line slope for the integrated equation when there is a large and lingering excess power effect [4]. The excess power present (0.038 W) prior to the cooling shown in Fig. 5 would likely be too small to detect such effects.

A dark film on the palladium cathode is generally observed for experiments conducted in $D_2O$ + LiOD solutions. However, for this lithium-free experiment conducted in $D_2O$ + $KNO_3$ the palladium cathode following this experiment showed the bright luster of palladium metal. This suggests that the black colorations on the cathode in lithium based electrolytes may be due to Li–Pd nitride compounds formed by the deposition of lithium metal onto the palladium cathode followed by reactions with nitrogen from the air introduced during the $D_2O$ additions.
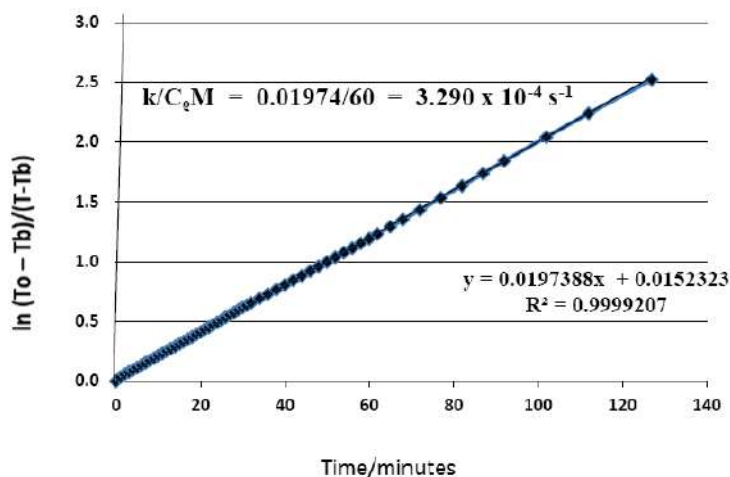


**Figure 5.** The experimental cell cooling expressed by the integrated equation (Eq. (9)).

## 6. Conclusions

The Fleischmann–Pons lower bound method provides a means of determining the heat transfer co-efficient for a calorimetric cell during an experiment while yielding accurate calorimetric results. Periods of large cell temperature changes with time are correctly modelled by the use of the Fleischmann–Pons differential equations. These calorimetric equations modified for heat transfer by conduction accurately describes the calorimetric experimental behavior of this Pd/$D_2$O+0.1 M $KNO_3$ experiment. This experiment showed that normal amounts of excess power (3.65 W/cm$^3$) can be obtained in a lithium-free electrolyte for the Pd/$D_2$O electrolysis system.

## Acknowledgements

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## Appendix A. Power Terms

*Electrochemical power*

$$P_{\text{EI}} = (E - E_{\text{H}})I. \tag{A.1}$$

*Heat radiation power*

$$P_R = -k_R(T^4 - T_b^4). \tag{A.2}$$

*Heat conduction power*

$$P_C = -k_C(T - T_b). \tag{A.3}$$

Heated gases ($D_2$, $O_2$, $D_2O$ vapor)

$$P_g = -(I/F)\left[0.5C_{p,D_2} + 0.25C_{P,O_2} + 0.75P'C_{p,D_2O}\right]\Delta T - 0.75(I/F)P'L, \tag{A.4}$$

where

$$P' = P/(P* - P) \quad \text{and} \quad P* = P_{D_2} + P_{O_2} + P_{D_2O} \approx P_{atm}.$$

*Pressure–Volume Work*

$$P_W = -0.75(I/F)RT \tag{A.5}$$

(see also M.H. Miles, *J. Condensed Matter Nucl. Sci.* **13** (2014) 392–400).

## Appendix B.  Cell Cooling For Radiative Heat Transfer

$$C_pM\,dT/dt = -k_R(T^4 - T_b^4), \tag{B.1}$$

$$\ln(T_0 - T_b)/(T - T_b) - \ln(T_0 + T_b)/(T + T_b) + 2\left[\tan^{-1}(T/T_b) - \tan^{-1}(T_0/T_b)\right] = 4T_b^3 k_R t/C_pM. \tag{B.2}$$

*Note*:

$$P_R = -k_R(T^4 - T_b^4) = -k_R\left[4T_b^3\Delta T + 6T_b^2\Delta T^2 + 4T_b\Delta T^3 + \Delta T^4\right],$$

where $\Delta T = T - T_b$.

## Comments of Referee 1

This paper is confusing because it describes the Fleischmann calorimeter and the equations applied by Fleischmann while using a different calorimeter to make measurements.

As several reviews of the Fleischmann method have shown, his method contains greater potential errors than he claimed. Nevertheless, the reviewers generally agree that the method was sufficiently accurate to support his claim for production of excess energy. Over the years, this method has been described and explained often enough that another description is not required. What is required in this paper is a detailed description of the method used here to obtain the claimed excess power, independent of what Fleischmann did 28 years ago.

Therefore, the Introduction should be rewritten and concentrate on what was done in this study without rearguing the history and merits of the Fleischmann method.

Presumably the calorimeter used here was the same one described in M. Miles, M. Fleischmann, Measurements of Excess Power Effects In Pd/$D_2O$ Systems Using a New Isoperibolic Calorimeter, *J. Condensed Matter Nucl. Sci.*

**4** (2011) 45–55 and M. Miles, Calorimetry, ARL Workshop, Adelphi, MD, 2010. If so, the physical shape and arrangement of the various internal components need to be described in the paper. Where exactly is the temperature measured? How stable is the temperature measurement? The author confuses the absolute accuracy (i.e. value relative to an universal standard), which is not important, with the stability of the temperature calibration over a period of time. What is the amount of noise on the value and the amount of drift over time. Thermistors are known to suffer from both sources of error.

Equation (1), as written, is very confusing. The goal of the study is to measure Px. Therefore, the equation should be written as equal to $P_x$. The heat capacity ONLY comes into play when temperature of the cell changes. During this time, the $\Delta T$ term would be slightly too small when the temperature is increasing and slightly too large when the temperature is decreasing. The $C_p$ term can be used to correct for this variation. On the other hand, less error is introduced if measurements of $P_x$ are only made when the temperature is constant. After all, excess power only has value if and when it is sustained as a steady source of power.

Assuming constant temperature: $P_x = k(T - T_b) + A$, where $k =$ (total power applied to the calorimeter)$/(T - T_b)$ and $A$ is a constant obtained by fitting $k$ to an equation over a range of applied power. Sine this is an open cell, the energy escaping as $D_2$ and $O_2$ gas needs to be added using the neutral potential. The terms $P_{gas}$ and $P_w$ are constants, hence are automatically corrected for by the calibration.

Because the calorimeter cannot measure the absolute amount of power, it must be calibrated as the author describes. Apparently, this calibration is achieved by calculating $k$ when no excess power being made by the sample. This value of $k$ is then used to determine the presence of excess power as being any apparent increase in power over what is called "the lower bound" value.

The description of charges in $k$ being caused by changes in the sources of power, such as that produced during loading, is confusing. The calibration constant is and must be a constant. It does not change. Once its value is obtained by calibration, it is then used to calculate any creation of power in excess that present during calibration.

In Fig. 1, the measurements are made so seldom, the time variation has no meaning. Should the points be connected as the author has done or should a line be drawn through the average, thereby assuming the variation results from random scatter in the measurement?

The description below Fig. 1, where the sluggish response of the oil is described, negates the heat capacity correction. This behavior, which is not typical of the Fleischmann calorimeter nor of any other needs to be acknowledged up front rather than confusing the reader initially with a description having no relationship to this behavior.

In fact, the heat capacity correction is very complex in this system. The energy originating at the cathode first transfers heat to the water, then energy reaches the glass container and the metal containing the oil before the proper temperature is achieved in the oil. Each of these heat sinks results in a different effective correction. Consequently, $C_p$ and $M$ are not known but have to be determined as variables based in the behavior of the system. This reviewer does not see how this determination is made.

The claim for heat production using $KNO_3$ instead of LiOD is important provided the claim can be believed. Unfortunately, the description does not give much confidence in the claim. Therefore, the paper needs extensive revision before it should be published.


**Response to Referee 1**

The comments of the first reviewer show the need for my discussion of the Fleischmann–Pons (F–P) calorimetry. This mathematically based calorimetry remains poorly understood by most scientists, and this includes many people involved with cold fusion such as this reviewer. Almost every comment by this reviewer illustrates the need to explain this F–P electrochemical calorimetry to those who have not taken the time to carefully study the F–P methods and equations. For starters, there are no valid reviews of this calorimetry that have found "greater potential errors" than

claimed. However, there are many erroneous comments and reviews of the F–P calorimetry.

First and foremost, the F–P calorimetry always introduces a differential equation based on the change of the cell temperature, $\Delta T = T - T_b$, with time $(d\Delta T/dt)$. The F–P method generally involves the application of this differential equation over two-day periods which include the use of an in-cell heater resulting in significant changes in the cell temperature with time. As shown by the differential equations of chemical kinetics, much more accurate results can be obtained by the mathematical integration of the differential equations. The F–P calorimetric differential equation is too complex to be directly integrated, thus numerical integration methods are applied (see my Ref. [6]). However, integration is possible when the cell is turned off giving a simpler differential equation, and the cell cooling closely follows the mathematical equations as shown in this paper.

There is never a time in cold fusion experiments using an open isoperibolic calorimeter where the cell temperature remains exactly constant (see my Ref. [14]). If the cell temperature actually remained constant, as proposed by this reviewer, then there would be no differential equations, no mathematical integrations and no F–P methods and equations. Two otherwise useful books by Ed Storms have promoted the error expressed by this reviewer regarding the need for the assumption of a constant cell temperature for isoperibolic calorimetry. This has led to false statements in these books about isoperibolic calorimetry such as "this method is hard to make accurate to better than $\pm250$ mW" and "correct power is only obtained when the temperature is constant".

The correct thermodynamic format for Eq. (1) is to place the power for the system $(C_p M\, d\Delta T/dt)$ on the left side and the sources of power into or out of the system on the right side as was always done by F–P. Anyone can algebraically rearrange Eq. (1) as desired.

This reviewer completely fails to understand the F–P "Lower Bound Method". This method always assumes that the excess power is zero, and the resulting "lower bound" cell constant, $k'$, is calculated. At the beginning of a Pd/$D_2$O experiment, this $k'$ may be near zero or even negative. The changes in $k'$, such as shown in Fig. 1, are explained by changes in the actual excess power as well as changes for $T - T_b$ (see my Eq. (6)) and not from "random scatter in the measurements".

The heat capacity for any isoperibolic calorimeter consists of all material within the cell up to the highest thermal barrier which controls the rate of enthalpy transfer into the constant temperature bath. For my heat conduction calorimetry, this includes the $D_2$O, the glass cell and electrodes, the heat transfer oil, and the inner copper tube. My experimental and calculated values for the heat capacity always show good agreement. The value for $C_p M$ will gradually decrease during electrolysis due to the loss of $D_2$O. The initial sluggish response of the oil is not unexpected because the heat transfer in the oil involves both conduction and convection, and convection may be somewhat slow in getting started when the experiment begins.

Finally, both the F–P Dewar calorimetry and my system are both isoperibolic calorimeters, and the same equations apply. The only difference is the main method of heat transfer. My calorimeter transfers most of the heat by conduction while the F–P calorimetry transfer most of the heat by radiation. All other calorimetric terms are exactly the same, and the same calorimetric methods and equations apply.

## Referee 2 Comments

The Fleischman–Pons isoperibolic base calorimeter design has been used for critical, extreme-precision, real-time energy balance studies on new battery Japanese technology for over 20 years. The base instrument function equations reiterated in the present paper are, in this reviewers view, unequivocal, and as well-tested and proven (under far more diverse conditions than those described in this paper) as any other known chemical reaction measurement technique. To this group's knowledge, there has never been any serious scientific challenge to the base master equations; there has been some serious misunderstanding of same, however, but this widely used calorimetric technique (and commercially available instrumentation) is well understood and remains above reproach. The author also seems to be

the most experienced researcher in this area, and is a known and respected thermodynamics expert.

As regards the verisimilitude of the claims of the experiment, this reviewer would ask what is to be gained in raising the controversy of an excess energy generation phenomena with a calorimeter that is modified in function *apropos* that of the Fleischman–Pons device that was used originally and which is already well-characterized? Specifically, the conduction pathway for heat transfer is indeed used in traditional commercial isoperibolic calorimeters with known reliability, but this pathway was evidently purposely avoided in the Fleischmann–Pons device. It then remains to resolve this question along with the fact that according to all available records, there was never any detection of excess thermal energy by Fleischman–Pons using the isoperibolic calorimetric technique with (a) palladium anode, platinum cathode; (b) any other anion other than deuteroxide; (c) any other cation other than lithium-6 or -7, and (d) any other solvent other than anhydrous (H) deuterium oxide; these were evidently often used as control variables by Fleischman and Pons

Besides providing evidence for a new chemical system under electrolysis that exhibits excess enthalpy, in contradiction to previous results in (b) and (c), we have to consider same is provided by use of a calorimeter that is apparently modified in thermal transfer mechanism to that used to provide the original and contradicting results. In addition, simultaneous (null) calibration results, while referred to in the text for a previous point in time, are not conveniently described or presented for comparison.

While the mathematical description is clear and accurate, the plausibility of the experiment is certainly believable, and there is no apparent reason to doubt the accuracy or integrity of the interesting results, there is reluctance to accept the conclusions of a new excess energy system made with a new hybrid energy transfer path calorimeter without at least providing (1) comparative null results under identical conditions as the present results in the same calorimeter, OR (better) (2) providing the results of the new system in a pure radiative isoperibolic Fleischman–Pons calorimeter.

## Response to Referee 2

I have no disagreements with this reviewer, but I have a few comments. I worked with three F–P Dewar calorimeters at NHE in Japan in 1997–1998, and I agree that this calorimetry is superior to any other calorimetry that I have used. However, I had very little government support for my cold fusion research following the ending of the U.S. Navy program in 1995. Furthermore, I did not know of any group capable of producing the F–P Dewar glass cells with silvering at the top. Therefore, I found a simpler and less expensive calorimetry design which involved heat conduction across inner and outer copper tubes completely separated by insulation. Incidentally, I asked for the three F–P Dewar calorimeters that I used in Japan when the NHE program ended in 1998, but permission was refused for my taking these calorimeters back to the U.S.

My F–P Dewar calorimetry used in Japan included three co-deposition experiments using the $ND_4Cl$–$ND_4OD$–$PdCl_2 + D_2O$ electrolyte. Significant excess power was observed in all three cells. There were no lithium-6 or lithium-7 cations in these palladium co-deposition experiments. Also, $Cl^-$ was the major anion and not $OD^-$ considering that the deposition of $Pd^{++}$ results in an acidic solution. Therefore, the observation of excess power using the F–P Dewar calorimetry apparently is not restricted to the use of $Li^+$ cations and $OD^-$ anions in the $D_2O$ electrolyte.

I discussed the design of my copper calorimeters with Martin Fleischmann, and his main reason for favoring the Dewar design was that there were no memory effects. Photons directly radiate heat between the Dewar cell and the water bath. For heat conduction calorimeters, the heat may linger inside the insulation. Also heat convection across the oil may vary somewhat with time. I have added to the experimental section to explain this calorimeter and to reference previous experiments where this same calorimeter was used. The main reason for my use of $KNO_3$ as an electrolyte was the opinion of Navy scientists at NRL that my excess power in the co-deposition experiments at NHE could be explained by the formation and reactions of nitrates. My report of no excess power in a $Pd/H_2O + KNO_3$

control experiment served as my experimental rebuttal. Furthermore, I had done extensive research on the $LiNO_3$–$KNO_3$ molten salt electrolyte which showed the excellent electrochemical stability of nitrate systems even at high temperatures.

I found this reviewer's report of the F–P Dewar calorimetry being used for accurate studies of new Japanese battery technology extremely interesting. If this became widely known, it could have a belated positive impact on the acceptance of the F–P cold fusion calorimetry.