Research Article

New analysis of MIT Calorimetric Errors

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Abstract

Accurate isoperibolic calorimetry requires a well-defined heat transfer pathway from the calorimetric cell to a constant temperature water bath. The MIT isoperibolic calorimetric results published in 1990 had a major impact in convincing scientists, as well as US Patent officials, that the anomalous excess enthalpy reported in 1989 by Fleischmann and Pons in Pd/D systems was due to various calorimetric errors. Additional information about the MIT calorimetry has allowed a more detailed analysis. The major new finding is that the walls of the MIT calorimetric cell were so well insulated with glass wool (2.55 cm thickness) that the major heat transfer pathway was out of the cell top into the room air rather from the cell into the constant temperature water bath. This helps to explain the reported sensitivity of 40 mW for the MIT calorimetry versus the sensitivity of 0.1 mW achieved for the Fleischmann–Pons Dewar calorimetry. The evaluation of calorimetric designs, accuracy of temperature measurements, electrolyte level effects, calorimetric equations, and data analysis methods leads to the clear conclusion that the Fleischmann–Pons calorimetry was far superior to that of MIT. Therefore, the results of the MIT calorimetry cannot be used as a refutation of the Fleischmann–Pons experiments.
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1. Introduction

The calorimetric results of MIT [1], Caltech [2], and Harwell [3] reported in 1989–1990 had a major impact in convincing most scientists that the anomalous excess enthalpy reported by Fleischmann and Pons [4,5] in Pd/D electrolysis systems was due to calorimetric errors. However, there were major errors in the Caltech, Harwell and MIT calorimetry that have been documented in a previous publication [6]. Critical experimental data was lacking in the initial MIT publication [1] that was later provided in a MIT report [7]. This additional information has allowed a more detailed analysis of the MIT calorimetry. The need for a new analysis of the MIT calorimetry even after 20 years was illustrated by a last minute book cancellation in 2010 by the American Institute of Physics (AIP) because someone apparently did not like the subject matter [8]. Furthermore, the US Patent office continues to block applications that mention the word cold

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fusion. Finally, the scientific journal access for Low Energy Nuclear Reactions (LENR) or cold fusion remains severely limited by the editors of refereed publications. This is all a lingering effect from the 1989 to 1990 reports from MIT, Caltech, and Harwell. A previous study concluded that the MIT calorimetric methodology was flawed and that this flawed MIT publication may be the single most widely quoted work used by the critics of cold fusion to dismiss the phenomena [9].

2. MIT Calorimetric Errors

2.1. Thick glass wool insulation

The major MIT calorimetric error is that the walls of the calorimeter were so well insulated with glass wool (2.55 cm thickness) that the major heat transport pathway was out of the cell top into the room temperature air rather than from the cell into the constant temperature water bath. The walls of any heat conduction calorimetric cell could be insulated to the point that almost all heat flow would be out of the cell top. Design calculations should be made prior to the calorimetric cell construction to determine the optimum amount of insulation to be used.

The dimensions of the MIT calorimeter were 7.60 cm in diameter and 15 cm in length while the glass cell had a diameter of 2.50 cm [1,7]. This leaves a space of 2.55 cm thickness that was filled with the glass wool insulation. For the radial heat flow from the cell, across the insulation, to the water bath, it can be shown [10] in terms of power (P) that

$$P = 2\pi k_i L(T_a - T_b)/\ln(r_b/r_a) = k_{\text{wall}}(T_c - T_b), \tag{1}$$

where k_i is the thermal conductivity of the glass wool ($0.040\,\text{Wm}^{-1}\text{K}^{-1}$), L the length (0.15 m), r_b the radius of the calorimeter (3.80 cm), r_a the radius of the glass cell (1.25 cm), $T_a = T_c$ the temperature inside the glass cell, and T_b is the temperature of the water bath. Therefore, the conductive heat transfer coefficient for the cell wall [7] is

$$k_{\text{wall}} = 2\pi k_i L/\ln(r_b/r_a) = 0.034\,\text{W/K}. \tag{2}$$

Based on the MIT experimental data reported [1,7] $T_c = 46.0°C$, $T_c - T_b = 20.0°C$, and $P = 1.76$ W, thus the cell wall transports only 0.68 W of power under these conditions

$$P = k_{\text{wall}}\Delta T = (0.034\,\text{W/K})(20\,\text{K}) = 0.68\,\text{W} \tag{3}$$

and only 39% of the total power (1.76 W) can be transferred across the cell wall due to the thick glass wool insulation. The MIT cell schematic shows about the same thickness of glass wool at the cell bottom, hence only about 0.06 W of power can be transferred across the cell bottom. The remainder of the power (1.76 W–0.68 W–0.06 W = 1.02 W) must be transferred across the cell top to the room temperature air. In summary, only 39% of the power for the MIT calorimeter is transferred across the cell wall to the water bath while 58% of the cell power is transferred across the cell top to the room temperature air. The remainder (3%) is transferred across the cell bottom. This undesirable result is due to the use of too much glass wool insulation.

Individual heat transfer coefficients can be calculated for the heat transfer across the cell top, across the cell walls, and across the cell bottom. Thus $k_{\text{top}} = 0.051$ W/K, $k_{\text{wall}} = 0.034$ W/K, and $k_{\text{bottom}} = 0.003$ W/K. The sum of these three pathways gives the total heat transfer coefficient for the MIT calorimetric cell as $k_{\text{total}} = 0.088$ W/K. This rather low value reflects the effect of the thick glass wool insulation that was used.

The use of a glass wool thickness of about 0.5 cm instead of the 2.55 cm thickness would have given much better results for the MIT calorimeter. This would have allowed a much higher percentage of the heat transfer to occur across the cell walls to the constant temperature water bath. For this 0.5 cm thickness of glass wool, k_{wall} would increase to 0.112 W/K and allow most of the cell power to be transported across the cell walls to the constant temperature water bath.

From the reported cell voltages and currents used in the MIT experiment, the electrochemical input power (P_{EI}) was only about 0.26 W. This means that about 1.50 W of heat power (P_H) was required to maintain a cell temperature of 46.0°C. It is unusual to use a cell heater power that is significantly larger than the applied electrochemical power, and this would make the detection of any excess power more difficult. For example, excess power is often only 10–20% of the input electrochemical power. The normally expected excess power would, therefore, be in the range of 26–52 mW. Considering the calorimetric error for the MIT system, such small excess power effects would have been difficult to detect. The small electrochemical input power of 0.26 W in the MIT experiments is due to the use of 0.25 M LiOD [1] rather than 0.10 M LiOD as in the Fleischmann–Pons experiments.

2.2. Room-temperature variations

Because most of the heat transfer is out of the cell top in the MIT calorimeter, the effect of room temperature variations will be greatly magnified. From the reported room temperature variations of ±2°C (Ref. 7), this error can be calculated as

$$\Delta P = k_{top} \Delta T = (0.051 \text{ W/K})(\pm 2\text{K}) = \pm 0.102 \text{ W}. \tag{4}$$

The MIT analysis of errors caused by room temperature variations gives a smaller error of ±0.044 W [7]. A simple method to minimize this error would be the use of less insulation for the cell walls to allow greater heat flow into the water bath. Furthermore, insulation could be added at the cell top to block the heat transfer to the room. In addition, accurate isoperibolic calorimetry requires much better control of the room temperature than reported by MIT. For example, a second thermal impedance unit can be used surrounding the cell and bath with a temperature control of better than ±0.2 K. These methods have proven to be successful in other calorimetric designs [1–14].

2.3. Temperature measurements

The reported accuracy of temperature measurements for the MIT calorimeter was ±0.1°C[1,7]. In contrast, the accuracy of temperature measurements in the Fleischmann–Pons Dewar cells was ±0.001°C[13,15]. This accuracy required careful internal calibrations of the thermistors. The electrochemical cells behave as well-stirred tanks, and the ultimate accuracy of the calorimeter is limited by the accuracy of the temperature measurements [13,15]. Thus, the temperature measurement accuracy of the Fleischmann–Pons calorimetric cells offers a one hundred fold increase in accuracy over the MIT calorimetric cell. This is consistent with the reported sensitivity of 40 mW for the MIT calorimetry [1,7] versus the sensitivity of 0.1 mW achieved for the Fleischmann–Pons Dewar calorimetry [15,16].

Temperature measurement errors can produce large errors in the power term for the calorimetric system or cell

$$P_{calor} = C_p M dT_c/dt, \tag{5}$$

where $C_p M$ is the heat capacity of the calorimetric system (J/K) and dT_c/dt is the rate of change (K/s) of the temperature of the cell [12,13]. From the reported size of the MIT cell [1,7] it is estimated that $C_p M = 300$ J/K, thus making a measurement every 300 s with a temperature error of ±0.1 K, could produce an error in P_{calor} of (300 J/K)(±0.1 K)/300 s = ±0.100 W. In contrast, for the Fleischmann–Ponns cell with $C_p M = 450$ J/K, the temperature measurement error of ±0.001 K would produce an error in P_{calor} of only ±0.0015 W. The data averaging and integration methods used by Fleischmann reduces the total error to ±0.1 mW [15,16].

2.4. Effect of electrolyte level

It was reported for the MIT calorimetric cell that the addition of 5.0 mL of D_2O to the cell required an increase of 0.15 W in heater power to maintain the same cell temperature [7]. Therefore, the change in the conductive cell heat transfer

coefficient with change in the electrolyte volume for the MIT calorimeter can be calculated as

$$\Delta k_c / \Delta V = 0.15\,\text{W}/(5.0\text{ mL})(20\text{ K}) = 0.0015\text{ W/K mL} \tag{6}$$

with $T_c - T_b = 20$ K. This effect of the electrolyte level for the MIT cell is significantly larger than measured for other calorimetric cells with the same diameter. This large electrolyte level effect for the MIT cell is due to the large heat flow out of the cell top rather than to the constant temperature water bath.

Recent measurements on a calorimetric cell with the same diameter as the MIT cell (2.50 cm), but with ample insulation at the cell top has given a much smaller value of $\Delta k_c / \Delta V = 0.0002$ W/K mL [14]. The change in power per mL of electrolyte volume is given by $\Delta P = (\Delta k_c / \Delta V)(T_c - T_b)$. For the MIT calorimeter where $T_c = 46.0°$C, $T_b = 26.0°$C, $\Delta P = 0.030$ W/mL. For our calorimeter with this same cell diameter and at the same temperatures $\Delta P = 0.004$ W/mL. The Fleischmann–Pons Dewar calorimeter at the same temperatures and cell diameter yields $\Delta P = (\Delta k_r / \Delta V)(T_c^4 - T_b^4) = 0.004$ W/mL. Kelvin temperatures to the fourth power are required for Dewar cells because the main heat transfer pathway is by electromagnetic radiation as expressed by the Stefan–Boltzmann law rather than by heat conduction as in the MIT calorimeter. Thus, the large heat flow out of the top of the MIT calorimeter produces an electrolyte level effect that is 7.5 times larger than other calorimeters of the same diameter.

The heat flow out of the cell top is also affected by the change in the thermal conduction path length (L) with change in the liquid level [7]. This can be expressed as [7]

$$P_{\text{top}}(t) = k_j A (T_c - T_{\text{top}})/L(t), \tag{7}$$

where k_j is the thermal conductivity of gases and other materials above the liquid level and A is the cross sectional area. It should be obvious that insulation at the cell top to block this heat flow pathway can greatly minimize this effect. Even if the heat flow out of the cell top were completely blocked, a small electrolyte level effect will remain for electrochemical calorimetric cells. This is due to the fact that the thermal conductivity of the gas phase is always smaller than that for the liquid phase within the cell. This can be expressed as

$$k_c = k_L (V_L / V_T) + k_G (V_G / V_T), \tag{8}$$

where k_c is the conductive heat transfer coefficient, k_L is the contribution for the liquid phase and k_G is the contribution of the gas phase. The volume of the liquid (V_L) and gas phases (V_G) can be used because their ratios to the total cell volume (V_T) are the same as the ratio of surface areas for all cells of the same diameter. Experimentally, it has been found that $k_G = 0.70\,k_L$ for cells with a diameter of 2.50 cm [13,14]. From Eq. (8), we obtain

$$dk_c / dV_L = k_L / V_T - k_G / V_T = (k_L - k_G)/V_T = k_L (1 - 0.70)/V_T, \tag{9}$$

where $dV_L = -dV_G$. Because $k_L > k_G$, there will always be a non-zero value for dk_c / dV_L even with zero heat flow out of the cell top. This effect, however, can be minimized by maintaining a constant surface area for the main heat transfer pathway from the cell electrolyte to the water bath. This is achieved in our present calorimeter by a secondary compartment containing a heat transfer fluid level that is always below the electrolyte level [14]. If the heat transfer fluid is always above the electrolyte level, experimental measurements yield $\Delta k_c / \Delta V = 0.0008$ W/K mL [14]. This is reduced to $\Delta k_c / \Delta V = 0.0002$ W/K mL by using a smaller amount of the heat transfer fluid such as its level is always below the electrolyte level. From Eq. 9, we calculate $dk_c / dV = 0.0006$ W/K mL for our cell where $k_L = 0.147$ W/K and $V_T = 70.0$ mL. The Fleischmann–Pons Dewar cell provides a constant radiative heat transfer area by silvering the top portion of their cell such that the electrolyte level is maintained within the silvered region [13,14]. Although the electrolyte level effect is not eliminated by these methods, it is certainly minimized. In contrast, the poor design of the MIT calorimetric cell maximizes the effect of the electrolyte level.

2.5. Missing calorimetric terms

The correct modeling of isoperibolic calorimetric systems involves eight different power terms [5,6,13–17]. These are the rate of changes of the enthalpy content of the calorimetric system (P_{calor}), the rate of enthalpy input due to the applied electrochemical current (P_{EI}), any applied heater power (P_H), excess power if present (P_X), the rate of enthalpy carried out of the cell by conduction (P_c) and by electromagnetic radiation (P_R), the rate of enthalpy transport out of the open cell due to the loss of the electrolysis gases and water vapor (P_G) and the rate of any work performed (P_W). Therefore, the first law of thermodynamics for the calorimetric system expressed as power can be stated as [16,17]

$$P_{calor} = P_{EI} + P_H + P_X + P_C + P_R + P_G + P_W, \tag{10}$$

where P_{EI}, P_H, and P_X are positive terms (rate of enthalpy added to the cell) and P_c, P_R, and P_G and P_W are negative terms (rate of energy transported from the cell to the surroundings). The power for the thermodynamic calorimetric system is represented by P_{calor} and defined by Eq. (5), thus Eq. (10) represents a differential equation. Exact expressions for each of these terms are presented elsewhere [5,6,13–16]. The expression for the rate of work done by the electrochemically generated gases (P_W) has not always been used [16,17], but this term is small and may often be neglected (see the Appendix).

The MIT calorimetric analysis [1] discusses the input power to the cell (P_{EI}), the heater power (P_H), the conductive thermal transport power (P_c) and excess power (P_X). There is no mention of the terms P_{calor}, P_R, P_G, and P_W. However, the missing P_R, P_G, and P_W terms would likely be small considering the low cell temperature (46.0°C and rather low cell current (195 mA). If the cell temperature had been maintained exactly constant, the P_{calor} term (Eq. (5)) would have been zero. However, the MIT temperature measurement error of ± 0.1 K could produce a large error of ± 0.100 W as discussed previously. The actual display of cell temperatures by MIT (Ref. 1, Figs. 4 and 5), shows a temperature error range of ± 0.25 K for the H_2O cell and a gradual increase of 0.5 K for the D_2O cell. Nevertheless, the MIT calorimetric analysis [1] certainly is better than the Caltech [2] or the Harwell [5] work in correctly identifying some of the more important terms needed for isoperibolic calorimetry.

3. Summary

A rather large error of 40 mW was reported for the MIT calorimetry. This large error is due mainly to the thick glass wool insulation that surrounded the walls of the MIT cells. As a result, the desired heat flow pathway from the cell to the constant temperature water bath was severely blocked, thus a major portion of the heat flow was through the cell top to the room temperature air. This created a large error source due to the large room temperature variations. Other contributing sources of error were the error in temperature measurements (± 0.1 K), a large electrolyte level effect, and missing calorimetric terms in the MIT calorimetric analysis. In contrast, the Fleischmann-Pons Dewar calorimetric cells provided for a constant radiative heat transfer pathway directly from the cell to the constant temperature water bath, much more accurate temperature measurements (± 0.001 K), a minimized electrolyte level effect due to a constant radiative heat transfer surface area, and the use of all required calorimetric terms in their data analysis. In addition, extensive data averaging and numerical integration of the calorimetric data in the differential equation was used to obtain an accuracy of ± 0.1 mW [13,15]. For any unbiased scientist, it should be clear that the Fleischmann–Pons calorimetry was far superior to that reported by MIT. Therefore, the MIT calorimetric results cannot be used as a refutation of the Fleischmann–Pons reports of anomalous excess energy in Pd/D systems.

A. Appendix

A.1. Role of work in electrochemical calorimetry

The First Law of Thermodynamics is expressed in terms of energy (U), heat (q) and work (w) where

$$\Delta U = q + w \tag{A.1}.$$

For pressure–volume ($P - V$) work done by the electrogenerated gases on the surroundings at constant pressure (P), $w = -P\Delta V$. From the Ideal Gas Equation, $PV = nRT$, the volume change is given by $\Delta V = \Delta nRT/P$, thus the work done by the electrolysis gases (D_2, O_2) is

$$w = -P(\Delta nRT/P) = -\Delta nRT. \tag{A.2}$$

The electrolysis of D_2O, $0.5\,D_2O \rightarrow 0.5\,D_2 + 0.25\,H_2$, produces 0.75 mol of D_2 and O_2 gases per Faraday (F). Therefore $\Delta n = 0.75\ It/F$, and the work done on the surroundings is given by

$$w = -0.75\,It\,RT/F. \tag{A.3}$$

In terms of power (P_W), this becomes

$$P_W = -0.75\,IRT/F. \tag{A.4}$$

Normally, this P_W term is small and could be included in the heat transfer coefficient by the calibrations. For example, at a current of $I = 0.100$ A, and a cell temperature of 50°C (323.15 K), $P_W= -0.0021$ W. Nevertheless, there could be an error if the cell is calibrated at $I= 0.100$ A, and the current is later increased to $I= 0.500$ A to give $P_W= -0.0105$ W at 50°C. Because of such possible changes in P_W, this term has been included in calorimetric equations in several previous publications [16,17]. This would account for the puzzling negative enthalpy (-436 J/day) reported for the Pd-B experiment on Day 61 when the cell current was increased to $I = 1.000$ A [13].

The use of enthalpy (H) in the calorimetric equations does not eliminate the need for the P_W term. Enthalpy is defined as

$$H = U + PV. \tag{A.5}$$

Thus at constant pressure, $\Delta H = \Delta U + P\Delta V$. If the only work is $P - V$ work, then $\Delta U = q$ - $P\Delta V$ and

$$\Delta H = q - P\Delta V + P\Delta V = q. \tag{A.6}$$

This is the well-known thermodynamic expression that ΔH at constant pressure equals the heat, q. The enthalpy change for the electrolysis reaction is used in calculating the thermoneutral potential, E_H, given by $E_H = -\Delta H/nF$. This thermoneutral potential is used in the term for electrolysis power, $P_{EI} = (E - E_H)I$. Although the $-E_H I$ term accounts for the rate of the chemical heat energy (q) present in the D_2 and O_2 electrolysis gases that leave the cell at constant pressure, it does not account for the rate of the work done by these gases on the surrounding atmosphere. This power term for work is given by Eq. (A.4).

Acknowledgements

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