



Research Article

# Examples of Isoperibolic Calorimetry in the Cold Fusion Controversy

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## Abstract

The Dewar isoperibolic calorimetry developed by Fleischmann and Pons can achieve an accuracy of  $\pm 0.1$  mW. This accuracy requires the use of seven power terms to adequately describe the rate of enthalpy flowing into and out of the calorimetric system. The isoperibolic calorimetry reported by Caltech, MIT, and Harwell neglected important power terms leading to large errors.

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*Keywords:* Caltech, Harwell, MIT, Power

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## 1. Introduction

The initial cold fusion controversy centered around claims by Fleischmann and Pons for anomalous excess enthalpy and excess power produced in Dewar-type isoperibolic calorimetric cells during the electrolysis of  $D_2O + LiOD$  using palladium cathodes [1]. This was soon followed by counter claims of no excess enthalpy produced in the calorimetric cells used by MIT, Caltech, and Harwell [2–4]. These and other examples will be examined in terms of the complete equation for isoperibolic calorimetry expressed by Eq. (??) [1,5,6].

$$P_{\text{calor}} = P_{\text{EI}} + P_X + P_H + P_C + P_R + P_{\text{gas}} + P_W. \quad (1)$$

The net power that flows into and out of the calorimetric system ( $P_{\text{calor}}$ ) is determined by the electrochemical power ( $P_{\text{EI}}$ ), excess power ( $P_X$ ), the internal heater power ( $P_H$ ), the heat conduction power ( $P_C$ ), the heat radiation power ( $P_R$ ), the power carried away by the gases generated ( $P_{\text{gas}}$ ), and the power due to pressure-volume work ( $P_W$ ). Each power term is a function of time ( $t$ ) such as  $P_{\text{calor}} = C_p M dT/dt$ , thus Eq. (??) is a differential equation that can be used directly or numerically integrated for greater accuracy. Equation (??), originally developed by Fleischmann and Pons, has not been challenged, yet many groups have not considered or have ignored important terms by making various approximations.

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## 2. Power Terms

### 2.1. Calorimetric System, $P_{\text{calor}}$

This is the thermodynamic system under consideration and usually consists mainly of the electrochemical cell, electrolyte, and electrodes. The rate of enthalpy flowing into or out of this system determines the rate of temperature change within the calorimeter. This term is modeled by the equation

$$P_{\text{calor}} = C_p M \, dT/dt, \quad (2)$$

where  $C_p M$  is the heat capacity of the system (J/K) and  $dT/dt$  is the rate of change of the cell temperature in degrees Kelvin per second (K/s). The heat capacity is expressed in the number of equivalent moles ( $M$ ) of  $\text{H}_2\text{O}$  or  $\text{D}_2\text{O}$  that would yield the correct total heat capacity, and  $C_p$  is the molar heat capacity of either  $\text{H}_2\text{O}$  or  $\text{D}_2\text{O}$  (J/mol K) [1,5]. At standard conditions, the molar heat capacities ( $C_p$ ) are 75.29 J/mol K for  $\text{H}_2\text{O}$  and 84.35 J/mol K for  $\text{D}_2\text{O}$ .

### 2.2. Electrochemical Power, $P_{\text{EI}}$

Power must be added to the cell to electrochemically change  $\text{D}_2\text{O}$  into  $\text{D}_2$  and  $\text{O}_2$  gases,  $2\text{D}_2\text{O} \rightarrow 2\text{D}_2 + \text{O}_2$ . Furthermore, the chemical energy contained in the  $\text{D}_2$  and  $\text{O}_2$  gases that flow out of an open isoperibolic calorimeter must be included in the calorimetric analysis. Thus, the equation for this term is given by [1,5–8].

$$P_{\text{EI}} = (E - E_{\text{H}}) I, \quad (3)$$

where  $E$  is the cell potential (V),  $I$  the cell current (A), and  $E_{\text{H}}$  is the thermoneutral potential (V) that is based on the chemical enthalpy of the  $\text{D}_2$  and  $\text{O}_2$  gases. In a closed isoperibolic cell with a recombiner, there would be no enthalpy carried out of the cell, thus  $P_{\text{EI}} = EI$ .

### 2.3. Excess power, $P_{\text{X}}$

This is the anomalous excess power that cannot be explained by recombination or any other chemical effects. It is often referred to as the Fleischmann–Pons Effect (FPE) excess power and generally requires the presence of both palladium and  $\text{D}_2\text{O}$  in electrolysis experiments [9,10].

### 2.4. Heat conduction power, $P_{\text{C}}$ , and heat radiation power, $P_{\text{R}}$

Heat can be carried out of the cell into the constant temperature water bath either by thermal conduction or by electromagnetic radiation that is mostly in the infrared region [8]. The cell construction determines the dominate heat transfer pathway. For cells with thermal insulation, heat conductance to the water bath should be the major pathway. For the Dewar cells with a good vacuum between the cell walls, the heat transfer should be mainly by electromagnetic radiation. The power term for the rate of enthalpy transferred by conduction is given by

$$P_{\text{C}} = -k_{\text{C}} (T - T_{\text{b}}), \quad (4)$$

where  $k_{\text{C}}$  is the conductive heat transfer coefficient (W/K), and  $T - T_{\text{b}}$  is the difference in the cell temperature and the bath temperature (K). Radiative heat transfer power is given by

$$P_{\text{R}} = -k_{\text{R}} (T^4 - T_{\text{b}}^4), \quad (5)$$

where  $k_{\text{R}}$  is the radiative heat transfer coefficient (W/K<sup>4</sup>) and both the  $T$  and  $T_{\text{b}}$  temperatures must be expressed in Kelvin, K. The radiative heat transfer coefficient can be estimated using the Stefan–Boltzmann constant

( $5.670373 \times 10^{-8} \text{ Wm}^{-2} \text{ K}^{-4}$ ) and the surface area of the Dewar cell [5,11]. Prior to the calorimetric cell construction, calculations should be made to determine the appropriate cell dimensions and the amount of cell insulation or Dewar-cell surface area that will ensure that the main heat transfer pathway is from the cell to the constant temperature water bath and not through the cell top to the room or through any other unwanted pathway. The clear advantage of the Dewar cell is that it allows visual observations inside the cell.

### 2.5. Other power terms ( $P_H$ , $P_{\text{gas}}$ , $P_W$ )

The heater power term,  $P_H$ , is simply the exact power in watts supplied by the resistance heater when it is operating. A typical value for the heater power is 0.2500 W [5].

The most difficult power term to express by an equation is  $P_{\text{gas}}$  [1,5,6,11]. This term includes the power carried out of the cell by the transport of the heated  $\text{D}_2$  and  $\text{O}_2$  gases as well as by the  $\text{D}_2\text{O}$  vapor. The power required for the vaporization of  $\text{D}_2\text{O}$  makes the largest contribution to this term [8,11]. This complicated power term is generally small except when the cell temperature exceeds about  $70^\circ\text{C}$  [5,8]. It can, however, become very large for cells driven to boiling [5, 8]. The complete equation for the  $P_{\text{gas}}$  term is given in Appendix A.

The power term for the rate of pressure–volume work done by the electrolysis gases is given by.

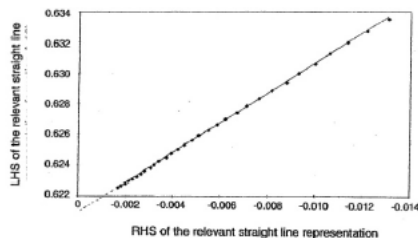
$$P_W = -RT (0.75 I/F) \quad (6)$$

assuming ideal gas behavior [8,12]. The 0.75 is the total number of moles of electrolysis gases produced by one Faraday (96,485 C) of current,  $R$  is the molar gas constant (8.3145 J/mol K) and  $T$  is the cell temperature (K). This power term is small and often neglected. However, it can produce an error if the calorimetric cell is calibrated using a small current and then a much larger electrolysis current is applied. For example, this term is  $-3.1 \text{ mW}$  for  $I = 0.150 \text{ A}$  at 323 K and increases to  $-20.9 \text{ mW}$  for  $I = 1.000 \text{ A}$  at this same temperature. The neglect of this term gave an erroneous small negative excess power of  $-5.0 \text{ mW}$  for Day 61 of the NHE Pd–B study [5]. Negative experimental excess power results were very rare for the accurate Fleischmann and Pons Dewar calorimetry, and the only adequate explanation was that the excess power was nearly zero and the  $P_W$  term had become significantly more negative when the cell current was increased to 1.000 A on Day 61 [5]. The negative quantities in Eqs. (??)–(??) have their usual thermodynamic significances in showing that the power or heat is transferred from the system to its surroundings.

### 3. Fleischmann–Pons Dewar Calorimetry

Fleischmann and Pons had perfected their isoperibolic Dewar calorimetry over at least five years prior to their 1989 announcement. This included the determination of the best size and shape of their calorimetric cell, attaining a good Dewar vacuum, improving their temperature measurements, acquiring good instrumentation, setting up a reliable data acquisition system, modeling their calorimetry with correct equations, and, especially important, improving their methods for the analysis of the calorimetric data. Improvements continued after 1989 such as the silvering of the top portion of their calorimetric cell that provides a constant radiative heat transfer surface from the liquid electrolyte to the water bath [12]. It should not be surprising that the limited cold fusion research by MIT and others fell far short of the calorimetric accuracy obtained by Fleischmann and Pons [1,12].

The calibrated thermistors used for temperature measurements by Fleischmann and Pons were accurate to  $\pm 0.001 \text{ K}$ , cell voltages were measured to within  $\pm 0.0001 \text{ V}$ , and current measurement were reported to within  $\pm 0.00001 \text{ A}$  [5]. The limiting accuracy, therefore, was the measurement of the cell temperature. Based on a 10 K difference in cell and bath temperatures, the calorimetric accuracy should approach  $\pm 0.01\%$ . This accuracy was attained where an experiment with 800 mW of input power was capable of measuring the power output to within  $\pm 0.1 \text{ mW}$  [13]. Besides very accurate measurements, methods of data analysis were perfected to reach this high accuracy. This included the use of averaging



**Figure 1.** Straight-line from backward integration of calorimetric data (see Fig. 8 of Ref. [13]).

methods for the data, casting the calorimetric equation into a straight-line form, and the numerical integration of the calorimetric differential equation [5,11,13]. No other group or calorimetric system has come close to the  $\pm 0.1$  mW precision and accuracy of the Fleischmann–Pons isoperibolic Dewar system. It was found that backward integration that includes the internal heater period yields the best results [5,13]. The heat capacity of the system ( $C_p M$ ) is obtained from the slope of the straight line, and the line intercept accurately gives the radiative heat transfer coefficient,  $k_R$ , to five significant figures [5,13].

An example of the straight line obtained from the backward integration of the calorimetric data for a platinum/D<sub>2</sub>O control experiment is shown in Fig. 1. This line is in the form  $y = C_p M x + k_R$ , and Fig. 1 shows the left-hand side (LHS) versus the right-hand side (RHS). The line intercept at  $x = 0$  yields  $k_R = 0.620187 \times 10^{-9}$  W/K<sup>4</sup> and the slope of this line yields  $C_p M = 341.1$  J/K [13]. For this graphical representation, the straight-line equation was modified by an estimate of  $C_p M$  to give a slope of near unity instead of the large slope equal to  $C_p M$ . The mathematical details of Fleischmann’s straight-line method are given in Appendix B. Many other examples of these methods are given elsewhere [5,11,13].

Claims of large errors for isoperibolic calorimeters are not valid as long as the measurements of the cell temperature, cell voltage and cell current are accurate. Reported calorimetric errors often trace back to the failure to consider all of the power terms presented in Eq. (??) or to poor cell designs. Adequate stirring by the electrolysis gases requires tall and narrow cells as used by Fleischmann and Pons. Typical cell dimensions were 25.0 cm in height with an inner diameter of 2.5 cm for Dewar cells [5]. The cathode and anode should be positioned near the bottom of the calorimetric cell to provide the best stirring by the electrolysis gases. The data analysis methods used for isoperibolic calorimetric results may also lead to different conclusions. This is generally due to errors in determining the key calorimetric parameters involving the conductive heat transfer coefficient,  $k_C$ , the radiative heat transfer coefficient,  $k_R$ , and the heat capacity of the calorimetric system,  $C_p M$  [5, 6]. In response to stirring questions, as many as seventeen thermistors were placed at various locations within the cell, and all gave the same temperature readings when properly calibrated [14]. Typically two thermistors are used in each cell [5,6]. In many isoperibolic calorimetric measurements reported, the important  $P_{\text{calor}}$  term is ignored. This term, however, can be large at the beginning of an experiment, when additional D<sub>2</sub>O is added, when the cell heater is operating, when the cell voltage is changing, or when the cell current is changed. There is no steady state where  $dT/dt = 0$  exactly, thus the  $P_{\text{calor}}$  term cannot be ignored. The use of the  $P_{\text{gas}}$  term requires the measurement of the atmospheric pressure in the laboratory (see Appendix), but this has seldom been reported. In short, the reports of large errors for isoperibolic calorimeters are, in fact, errors made by those conducting such experiments

The largest experimental measurement error in the Fleischmann–Pons Dewar calorimetry resides in the cell temperature measurement. This temperature error can be used to calculate how this error limits the calorimetry. This is done by using Eq. (??) and assuming a typical radiative heat transfer coefficient of  $k_R = 0.8000 \times 10^{-9}$  W/K<sup>4</sup>, a bath temperature of 298.150 K (25°C), and a cell temperature of 313.150 K (40°C). Results are shown in Table 1.

For the Fleischmann–Pons temperature error of  $\pm 0.001$  K, the resulting calorimetric error would be  $\pm 0.1$  mW as experimentally determined [13]. This calorimetric error increases to about  $\pm 1.0$  mW for the cell temperature error of  $\pm 0.01$  K and to about  $\pm 10$  mW if the cell temperature error is  $\pm 0.1$  K. Similar calorimetric errors due to cell temperature measurements are found with heat conduction calorimeters if  $k_C = 0.1000$  W/K. These limiting errors will be smaller for smaller calorimeters that have smaller heat transfer coefficient, but the smaller cell size results in a larger electrolyte level effect error. Trade offs are necessary in the dimensions of the calorimetric cell.

#### 4. Caltech, MIT, and Harwell Calorimetric Errors

The Caltech, MIT, and Harwell calorimetric errors have been fully documented in previous publications [6,12], thus this is only a brief summary.

The Caltech isoperibolic calorimetry publications show only fragments of Eq. (1), thus only  $P_{EI}$  and a term for the total power similar to  $P_C$  could be identified. The Caltech cell required electrical stirring due to its large diameter, and this introduced a poorly defined heat source. The most disturbing aspect of the Caltech experiments was that the cell constant was arbitrarily allowed to change with time. This alone will serve to zero out any possible excess power [6]. The MIT isoperibolic calorimetry used terms corresponding to  $P_{EI}$ ,  $P_H$ , and  $P_C$  in Eq. (??) and  $P_{calor}$  would be small or zero in their constant temperature system. However, a large error in the MIT calorimetry was that the major heat transfer pathway was out of the cell top due to the thick glass wool insulation that was used for the cell walls [12]. Temperature measurements accurate to only  $\pm 0.1$  K were also a large source of error for the MIT calorimetry. The Harwell isoperibolic calorimetry shows only the use of the  $P_{EI}$  term and approximations for  $P_{gas}$ ,  $P_R$ , and  $P_C$ . Other error sources include their method of cell calibration and the unfavorable geometry of various cathodes used [6].

In contrast to Caltech, MIT, and Harwell, the Grenoble work in France succeeded in obtaining excess power using Dewar cells [15]. The only power terms of Eq. (??) neglected was the small  $P_W$  term. Five out of 18 experiments by the Grenoble group produced excess enthalpy. The measured excess power ranged from 50 to 300 mW and the percent of excess power reached 150% during the boiling phase [15].

The actual power terms used by various groups in their isoperibolic calorimetry is shown in Table 2.

The power terms for heat conduction ( $P_C$ ) could be left out for the three groups using Dewar calorimetric cells

**Table 1.** Effects of cell temperature errors

$T_C$ (K)	$\Delta T_C$ (K)	$P_R$ (W)*	$\Delta P_R$ (W)
313.150	–	1.37144	–
313.151	0.001	1.37154	0.00010
313.160	0.010	1.37242	0.00098
313.250	0.100	1.38127	0.00983
314.150	1.000	1.47018	0.09874

\*Assuming  $k_R = 0.8000 \times 10^{-9}$  W/K<sup>4</sup> and  $T_b = 298.150$  K.

**Table 2.** Calorimetric power terms reported

Group	$P_{calor}$	$P_{EI}$	$P_X$	$P_H$	$P_C$	$P_R$	$P_{gas}$	$P_W$
F–P *	Yes	Yes	Yes	Yes	–	Yes	Yes	No
Miles	Yes	Yes	Yes	Yes	Yes	–	Yes	Yes
Caltech	No	Yes	No	No	Yes	–	No	No
MIT	No	Yes	No	Yes	Yes	–	No	No
Harwell	No	Yes	No	No	–	Yes	No	No
Grenoble	Yes	Yes	Yes	Yes	–	Yes	Yes	No

\*Fleischmann–Pons.

(Fleischmann–Pons, Harwell, and Grenoble). Similarly, for the three groups using heat conduction calorimetry (Miles, Caltech, MIT), the power terms for radiation ( $P_R$ ) could be ignored. It is obvious from Table 2 that the three groups that reported no excess power (Caltech, MIT, and Harwell) failed to include several power terms in their analysis. For Caltech, the power terms  $P_{\text{calor}}$ ,  $P_H$ ,  $P_{\text{gas}}$ , and  $P_W$  were not discussed. The MIT calorimetry failed to mention  $P_{\text{calor}}$ ,  $P_{\text{gas}}$  and  $P_W$ . Harwell missed the  $P_{\text{calor}}$ ,  $P_H$ ,  $P_{\text{gas}}$  and  $P_W$  power terms. In contrast, the Grenoble group left out only the small  $P_W$  power term.

## 5. The Thermoneutral Potential

Perhaps the most controversial term for open isoperibolic calorimetry is the use of the thermoneutral potential,  $E_H$ , in the  $P_{\text{EI}}$  power term (Eq. (3)). For the exothermic and spontaneous reaction at standard conditions,



the change in enthalpy (heat at constant pressure) is  $\Delta H^\circ = -294.600$  kJ per mol of  $\text{D}_2\text{O}$  produced [16]. Thus, the thermoneutral potential is given by

$$E_H = -\Delta H^\circ/2F = 1.52666 \text{ V}. \quad (8)$$

This is the potential at which the cell filled with  $\text{D}_2\text{O}$  could remain at standard temperature (298.15 K) during electrolysis without any heat exchange with its surroundings (thermoneutral). The actual cell potential during electrolysis is greater than  $E_H$ , and this adds heat to the cell. If one mole of  $\text{D}_2\text{O}$  is electrochemically converted into  $\text{D}_2$  and  $\text{O}_2$  gases that escape from the open cell, then the chemical enthalpy contained in these gases is given by  $\Delta H^\circ = -2FE_H = -294.600$  kJ. Suppose for example that the electrolysis current is 0.500 A. The rate of  $\text{D}_2\text{O}$  electrolysis is then  $2.5911 \times 10^{-6}$  mol/s ( $I/2F$ ). This yields  $-0.76333$  W ( $I\Delta H^\circ/2F = -E_H I$ ), thus the  $-E_H I$  term in Eq. (??) provides a convenient method for accurately calculating the chemical power carried out of the cell in the form of the  $\text{D}_2$  and  $\text{O}_2$  electrolysis products. There is no other potential except  $E_H$  that will exactly account for the rate of chemical enthalpy leaving the cell in the form of the  $\text{D}_2$  and  $\text{O}_2$  electrolysis gases. If these gases are recombined in a closed calorimetric cell, then this calculation is not required. Appendix C provides additional information about the thermoneutral potential.

Another controversial point often raised is that 100% of the current is not always used for  $\text{D}_2\text{O}$  electrolysis. This can be checked by measuring the volume of gases produced per unit time and comparing this with Faraday's law. An integrated method over the entire experiment is the measurement of the volume of  $\text{D}_2\text{O}$  that is consumed [10]. There may be other reactions such as recombination or oxygen reduction at the cathode that interfere with the  $\text{D}_2\text{O}$  electrolysis. Thus Eq. (??) could be modified to give

$$P_{\text{EI}} = (E - \gamma E_H) I, \quad (9)$$

where  $\gamma$  is the current efficiency for  $\text{D}_2\text{O}$  electrolysis. Our experiments have shown that  $\gamma$  is very close to 1.00 and can be neglected except for a few co-deposition studies. A control study using a platinum cathode in  $\text{D}_2\text{O}$  has reported the small value of  $1.1 \pm 0.1$  mW for recombination that is attributed to the electrochemical reduction of oxygen at the cathode [13]. This experiment used a current of 0.2000 A, thus the correction for the current efficiency yields  $\gamma = 0.9964$ . This small error is readily corrected by the cell calibrations [13].

## 6. Conclusions

The accuracy of electrochemical isoperibolic calorimetry should approach the accuracy of the cell and bath temperature measurements. For the Fleischmann–Pons isoperibolic Dewar calorimetry, this accuracy limit is  $\pm 0.01\%$  or  $\pm 0.1$  mW. The cold fusion controversy traces back to the poor calorimetry and methods of data analysis used in the Caltech, MIT

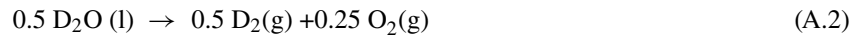
and Harwell studies. Important calorimetric terms were omitted in their experimental analyses. Even today, the reports of large errors for isoperibolic calorimeters are due mainly to the errors made by those conducting the experiments. These errors often include the neglect of important calorimetric terms, poor design of the calorimetric cells, large errors in temperature measurements, and inadequate analysis of the calorimetric data.

### Appendix A.

Another pathway for the transfer of enthalpy from the open cell to the surroundings is by the heated gases that vent from the cell top through a small glass exit tube. These gases are the electrolysis gases, D<sub>2</sub> and O<sub>2</sub>, as well as D<sub>2</sub>O vapor carried out of the cell. The evaluation of this enthalpy transfer requires the molar heat capacities of D<sub>2</sub> gas ( $C_{p,D_2}$ ), O<sub>2</sub> gas ( $C_{p,O_2}$ ), and D<sub>2</sub>O vapor ( $C_{p,D_2O(g)}$ ) as well as the enthalpy of vaporization (L) of D<sub>2</sub>O(L). The gas pressure within the cell,  $\mathbf{P}^*$ , is approximately equal to the atmospheric pressure in an open system. Using Dalton's law of partial pressure

$$\mathbf{P}^* = \mathbf{P}_{D_2(g)} + \mathbf{P}_{O_2(g)} + \mathbf{P}, \quad (\text{A.1})$$

where  $\mathbf{P}$  is the partial pressure of D<sub>2</sub>O gas at the cell temperature. The pressure terms are bolded to minimize confusing them with power terms. The electrolysis reaction per Faraday ( $F$ )



consumes 0.5 mol of D<sub>2</sub>O and produces a total of 0.75 mol of D<sub>2</sub> + O<sub>2</sub> gases. The amount of D<sub>2</sub>O<sub>(g)</sub> carried away per Faraday is then given by Eq. (A. 3)

$$\text{mol D}_2\text{O (g)} = 0.75(\mathbf{P}/(\mathbf{P}_{D_2} + \mathbf{P}_{O_2})) = 0.75(\mathbf{P}/(\mathbf{P}^* - \mathbf{P})). \quad (\text{A.3})$$

The rather complicated power term,  $P_{\text{gas}}$ , for the rate of enthalpy transfer by the gases leaving the cell is given by

$$P_{\text{gas}} = -(I/F)\{[0.5C_{p,D_2} + 0.25 C_{p,O_2} + 0.75 (\mathbf{P}/(\mathbf{P}^* - \mathbf{P})) C_{p,D_2O(g)}] \Delta T + 0.75 (\mathbf{P}/(\mathbf{P}^* - \mathbf{P}))L\}, \quad (\text{A.4})$$

where  $\Delta T = T - T_b$ . The first term multiplied by  $\Delta T$  represents the rate of enthalpy transfer by the D<sub>2</sub>, O<sub>2</sub>, and D<sub>2</sub>O gases leaving the cell. The second term multiplied by the heat of vaporization of D<sub>2</sub>O (L) represents the power for the change of D<sub>2</sub>O from a liquid to a gas. This second term makes the largest contribution to the  $P_{\text{gas}}$  power term [11]. Assuming  $I = 0.2000$  A and  $T_b = 22.00^\circ\text{C}$ , the  $P_{\text{gas}}$  term is -5.65 mW at  $T = 40.00^\circ\text{C}$  and increases to -57.83 mW at  $T = 80.00^\circ\text{C}$  [11]. As seen by Eq. (A.4), these numbers would be doubled for  $I = 0.4000$  A.

### Appendix B.

Martin Fleischmann's straight-line method begins with the calorimetric Eq. (??) expressed as

$$C_p M \, dT/dt = -k_R f(T) + P_{\text{net}} + P_X \quad (\text{B.1})$$

for Dewar cells where  $P_R \gg P_C$  and where  $P_{\text{net}} = P_{\text{EI}} + P_H + P_{\text{gas}} + P_W$  and  $f(T) = T^4 - T_b^4$ . Rearrangement of this differential equations yields

$$(P_{\text{net}} + P_X) \, dt/f(T) \, dt = C_p M \, dT/f(T) \, dt + k_R. \quad (\text{B.2})$$

Let

$$y = (P_{\text{net}} + P_X) dt/f(T) dt \quad \text{and} \quad x = dt/f(T) dt,$$

where  $y$  has units of  $\text{W/K}^4$  and  $x$  has units of  $\text{K}^{-3} \text{s}^{-1}$ . This gives a straight-line form for the differential equation

$$y = C_p M x + k_R. \quad (\text{B.3})$$

The substitution  $y = C_p M' y'$  where  $C_p M'$  is an estimated value for  $C_p M$  gives  $y'$  and  $x$  the same units ( $\text{K}^{-3} \text{s}^{-1}$ ), thus

$$C_p M' y' = C_p M x + k_R. \quad (\text{B.4})$$

Multiplying Eq. (B.4) by  $10^9$  removes the large exponents for each term, and numerical integration over a selected time period yields

$$10^9 C_p M' [y'] = 10^9 C_p M [x] + 10^9 k_R, \quad (\text{B.5})$$

where  $[y']$  and  $[x]$  represent numerically integrated values for these variables. At  $[x] = 0$ ,  $10^9 k_R$  equals the intercept value.

An advantage of this straight-line method is that possible errors from  $C_p M$  are eliminated at  $[x] = 0$ . The slope of the straight line is  $C_p M / C_p M'$  and is near unity when a good estimate of  $C_p M'$  is used. The actual heat capacity value is given by  $C_p M = (\text{slope}) (C_p M')$ . Various integration methods have been reported by Fleischmann [5,11,13], but backward integrations from the midpoint of the two-day cycle ( $t_2$ ), through the heating pulse, to near the beginning of the cycle ( $t$ ) gives the best results. Furthermore, the  $k_R$  value obtained is for the mid-point of the two-day cycle. The cell is refilled with  $\text{D}_2\text{O}$  at the beginning of each measurement cycle ( $t = 0$ ). Fleischmann's straight-line method assumes that the excess power ( $P_X$ ) is zero or constant over the selected time period. It is not possible to accurately calibrate any calorimetric system when the excess power is changing.

### Appendix C.

In addition to the heat carried out of the cell by the  $\text{D}_2$ ,  $\text{O}_2$ , and  $\text{D}_2\text{O}$  gases ( $P_{\text{gas}}$ ), there is also chemical energy contained in the  $\text{D}_2$  and  $\text{O}_2$  gases that could be obtained if they react outside the cell (see Eq. (??)). Therefore, in an open cell

$$P_{\text{EI}} = EI + (I/2F) \Delta H, \quad (\text{C.1})$$

where  $\Delta H$  is negative for Eq. (??). As usual, power added to the system (cell) is positive and power carried away from the system is negative. This equation using  $\Delta H$  ( $\text{J mol}^{-1}$ ) for the chemical reaction of  $\text{D}_2$  and  $\text{O}_2$  outside the cell can be used directly. However, it is more convenient to use the relationship  $\Delta H = -2F E_H$  (Eq. (??)) to obtain

$$P_{\text{EI}} = EI + (I/2F)(-2F E_H) = EI - E_H I \quad (\text{C.2})$$

or

$$P_{\text{EI}} = (E - E_H)I \quad (\text{C.3})$$

for these calculations. Note that at  $E = E_H$ ,  $P_{\text{EI}} = 0$ , and no heating effect is provided by the electrolysis (thermo neutral). Both Eqs. (C.1) and (C.3) will give exactly the same results. At standard conditions,  $E_H = 1.52666 \text{ V}$  for  $\text{D}_2\text{O}$  as given in Eq. (??) and  $1.48121 \text{ V}$  for  $\text{H}_2\text{O}$ . Thermodynamic equations (Kirchhoff's law) allow the calculation of  $\Delta H$  for other temperatures, thus also  $E_H$ . For example  $E_H = 1.52150 \text{ V}$  at  $50^\circ\text{C}$  for  $\text{D}_2\text{O}$  experiments.



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