# Some Lessons from 3 Years of Electrochemical Calorimetry

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## Abstract

An analysis of the time series data from the 16 Harwell FPH electrochemical cells is being conducted. Using generally accepted calorimetric principles and detailed numerical analysis, the behavior of "cold fusion" output data is used to estimate the instrumental sensitivity and the time varying accuracy of the results of the experiments. In Harwell's $D_2O$ Cell 3 there are more than ten time intervals where an unexplained power source or energy storage mechanism may be operating. A comparison to a previous analysis of Pons and Fleischmann data is made.

## Introduction

With the cooperation of Harwell and its research team, Williams et al[2], we have obtained copies of the digital data, laboratory notebooks, and other records of the 1989 Harwell electrochemical calorimetry experiments on "cold fusion". With this information we have been able to explore the characteristics of their experimental design and their data thereby developing insight into the quality of the experimental results. These results are briefly compared to results of Hansen's [1] similar analysis of Pons and Fleischmann data.

## Conclusions

- Characterizing the Instruments. Harwell's extensive variations in the timing and magnitude of the calibration heater power and the electrochemical current/voltage pose a robust test of models of the electrochemical calorimetry instrument.
- Experimental Protocol and Interpretability. The regularity of the experimental protocol used by Pons and Fleischmann as reported at ICCF2 by Hansen[l] produces significantly less ambiguity in interpretation of experimental results than those used by Harwell.
- Extractable Information. Regression techniques for estimating parameters in mathematical models can be applied to the Harwell data to extract more information than presented by Williams et al [2].

- Reliability of Data Sets. Not all operating regimes captured in the Harwell data can be described by the available models. However, performance over extensive time intervals are well described and can be used to accurately estimate heat transfer coefficients, anomalous power values, and experimental uncertainty.
- Anomalous Power in Cell 3. Heavy water Cell 3 showed a marked temperature rise on more than ten occasions while its light water control Cell 4 showed no such rise. The power required to generate these increased temperatures is 100-200 mW. The input power to the cell was generally less than 1500 mW. The calorimetric error during these periods was approximately 1%.

## Data Screening and Parameter Estimation

We have found in studying the Harwell data from their FPH cells that the accuracy to which they can be analyzed varies greatly from cell to cell and within a given cell. We have found that an effective way of finding "good" regions, i.e., those with small fluctuations in the estimated parameters, for analysis is to calculate the conductive heat transfer coefficient Kc using a "sliding" window of, say, ten points(30 min), which is moved over the entire time history of the cell. For this the excess heat, Qf, is temporarily assumed to be zero.

Plots of such running Kc values are shown in Figure 1a for heavy water Cell 5 and in Figure 1b for light water Cell 14. Cell 14 is obviously much better behaved than Cell 5. Ideally, Kc should remain constant. The large change with electrolyte height, the "tidal effect", is easily understood. The tidal variations and especially the wild gyrations are simply due to poor cell design and function.(Effects on performance and virtual elimination of the tidal variations in Pons and Fleischmann redesigned cells is described in Hansen [1].) Fortunately there is an abundance of FPH data, including many calibration pulses of known power. Sometimes the equations (Pons and Fleischmann equations are used here) don't fit the large changes in current and heater power, presumably because stirring ceases to be adequate or some other control breaks down. These regions become obvious from a study of apparent Kc behavior. But where Kc is somewhat misbehaved the fit is good and a non-zero Qf would show up clearly.
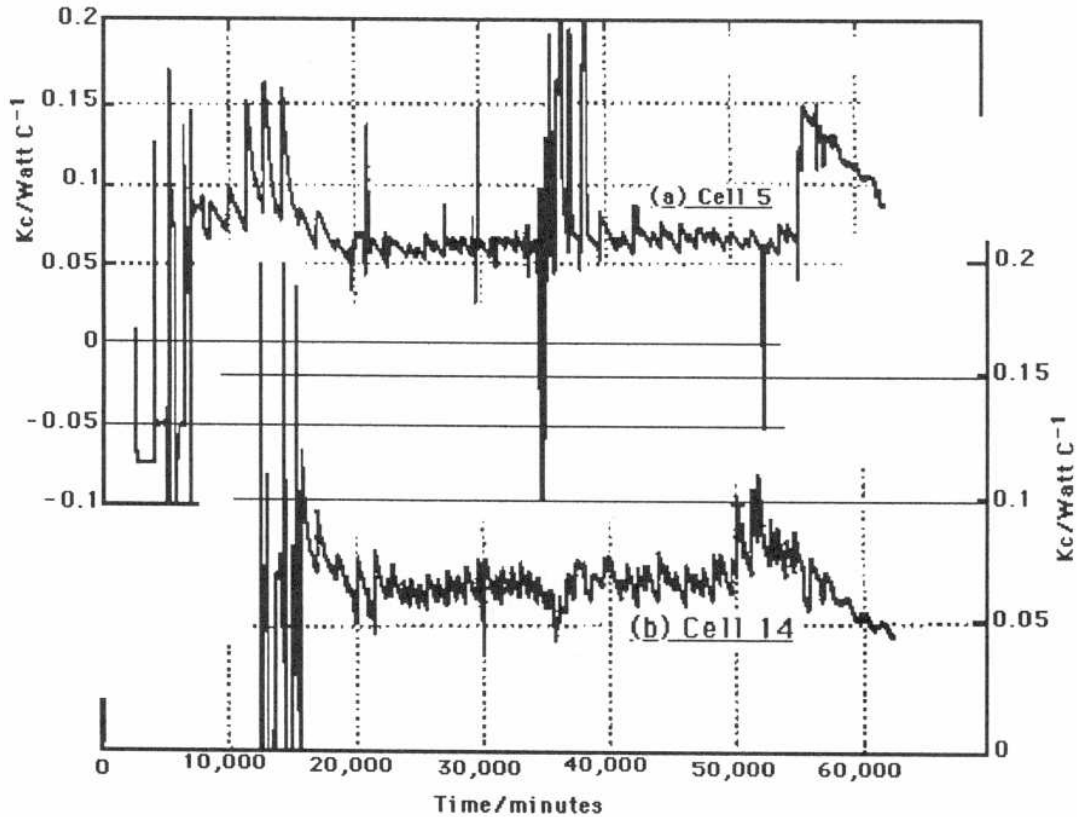
**Figure 1. Thirty minute "sliding window" estimates of the conductive heat transfer coefficient for: (a) 41 days of operation of $D_2O$ Cell 5; (b) 36 days of operation of $H_2O$ Cell 14.**

These observations are illustrated in the Figure 1 and Table 1. Cell 14 is fairly well behaved from data point 5,500 (18,850 min) out to 15,800 (49,750 min). The many pulses and current gyrations in this region" are well accommodated by the equations. In Cell 5, however, there are several regions where a reasonable fit cannot be achieved. It is simply fruitless to attempt fits in these regions. The data are faulty. Fits can still be had in good regions.

Table 1 shows the results of least squares optimization over various time intervals with simultaneous fitting of Kc and Qf. By choosing regions with calibration pulses and by avoiding a few bad regions, Qf can be determined to within about 0.01 watts. This is an order of magnitude better than the original analysis of these data presented by Williams [2].

**Table 1. Estimated Kc and Qf for H$_2$O Cell 14. (Kr = 5 × 10$^{-10}$ watts deg$^{-4}$)**

| Time/minutes | Kc/Watts C$^{-1}$ | Qf/ Watts |
|---|---|---|
| 18,850-21,850 | 0.0659 | -0.0072 |
| 20,500-23,350 | 0.0676 | 0.0028 |
| 23,350-25,350 | 0.0649 | 0.0091 |
| 29,350-32,350 | (Failed to converge, | no good calibration pulse.) |
| 33,850-36,850 | 0.0766* | 0.0621* |
| 38,350-41,350 | 0.0688 | -0.0083 |
| 18,850-35,350 | 0.0682 | 0.0143 |
| 18,850-62,350 | 0.0698 | 0.0064 |
| 41,350-62,350 | 0.0757** | 0.0206** |

**\* Suspect estimates, see Figure 1.**

**\*\* Data beyond 50,350 min is suspect, yet the estimate for average Qf is within 2% of zero.**

## Anomalous Power in Cell 3

Harwell Cells 1, 2, 3, and 4 were wired in series to a constant current source. Odd numbered cells had D$_2$O, even numbered cells H$_2$O. The Pd cathode of 6mm diameter by 10 mm length was in 0.1 molar NaOD in Cell 3 and 0.1 molar NaOH in Cell 4. Figure 2 shows a section of time series data covering the period 10,000 minutes to 30,000 minutes. The data collection started at 2,350 minutes and a 198 mA current was first applied at 2,632 minutes.

Compare the behavior of the temperature and input power traces for Cell 3 with those of Cell 4 starting at time 13,918 min, where the Cell 3 voltage jumps by 80 mV (not shown) and its temperature begins a much faster rise. The temperature rise is halted with the refilling of Cell 3 at time 14,197 min, which produces a voltage increase of 26 mV, while Cell 4 is refilled at 14,212 min producing a voltage drop of 39mV. The temperature change for Cell 3, T(14,197) - T(13,918) = 31.84 - 30.47 = 1.37 C; compare to Cell 4, T(14,212) - T(13,918) = 26.16 - 25.96 = 0.20 C. That is, over the same nearly 3 hour interval with the same electrical current in the same bath but with different electrolytes, Cell 3 experienced a 1.37/.20 = 6.85 greater temperature rise than Cell 4.

Subsequent to Cell 3's rapid temperature rise at 13,918 minutes it experiences a sequence of over 10 similar increases during the next 9 days. Throughout these anomalous increases in temperature in Cell 3, Cell 4 behaves "normally", i.e., it suffers no unexplained pulses of energy. Our initial estimate of the power associated with these anomalous temperature increases is 100-200 mW. The electrolytic current was under 300 mA and the potential was less than 5 V. There are calibration pulses which occur during these events. Further analysis of this data is warranted and underway.
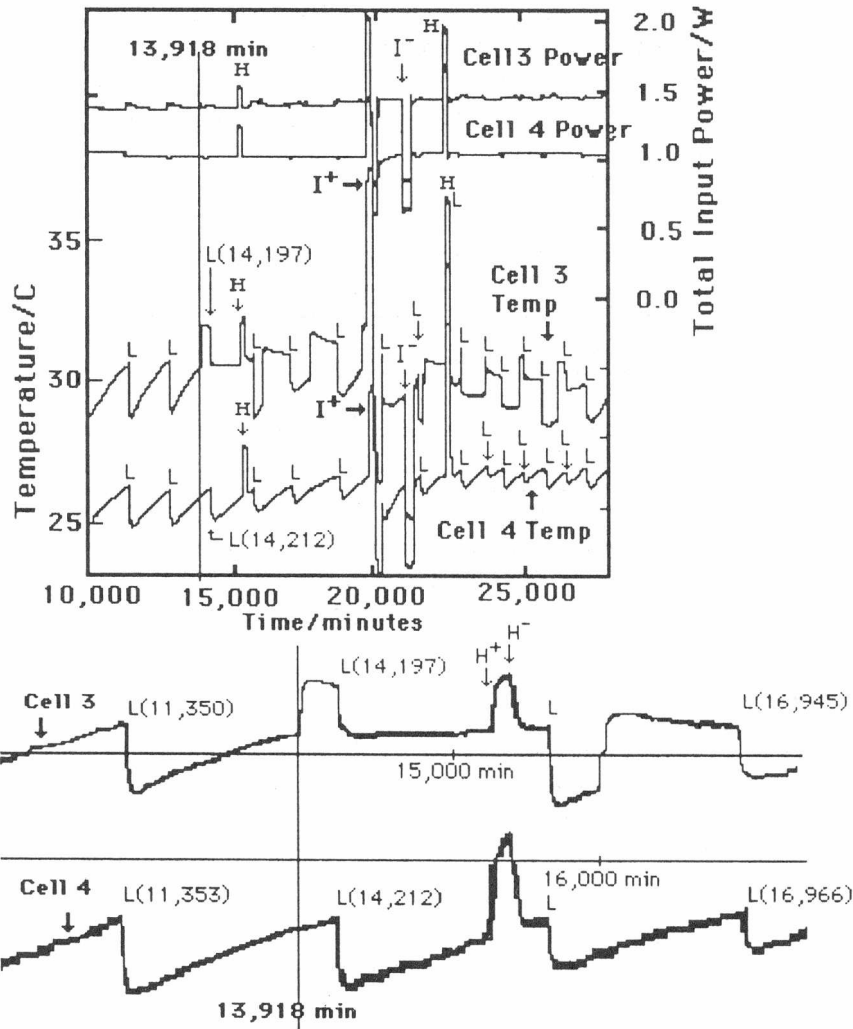
Figure 2. Temperature and total externally supplied input power for D$_2$O Cell 3 and H$_2$O over a 13 day period. L= liquid addition; H= heater pulse; 1= electrolytic current change. + = increase; - = decrease. Lover chart is an expansion of the temperature time series around the time 13,918 where Cell 3 shows a rise in temperature different from Cell 4.

## List of Symbols/Nomenclature

Kc - Conductive heat transfer coefficient, W/degree C

Kr - Radiative heat transfer coefficient, W/degree C$^4$

Qf - Excess Heat, W

Points - Data point set, collected every three minutes in Harwell experiments

T(14,198) - Temperature at time 14,198 since starting time of Harwell experiments, may not be from starting time of particular Cell

L; L(19,128) - Liquid addition; at the particular indicated minute, e.g., 19128 minutes

## References

1. Hansen, W.N., 1992, *Proceedings of the II Annual Conference on Cold Fusion, Vol. 33 of the Conference Proceedings*, The Italian Physical Society, Bologna, p. 491, http://lenr-canr.org/acrobat/HansenWNreporttoth.pdf
2. Williams, D.E., et al, *Nature,* 342 (1989), 375