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Pd/D CALORIMETRY - THE KEY TO THE F/P EFFECT AND A CHALLENGE TO SCIENCE

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Abstract

The main issue before this conference can be stated as a simple question:

Question #1: Can large amounts of heat be generated at a significant rate by Pd/D interaction as announced by Fleischmann and Pons?

By now there have been many experimental results claiming to answer "yes" and which force us to take that possibility very seriously. As used here the "large amounts" are much larger than can possibly be explained by chemistry or metallurgy as known today. Up to now the only practical way of answering this question is by Pd/D calorimetry. That being so, a second question naturally follows.

Question #2: Are there any Pd/D calorimetric data sets extant which are competent to clearly answer Question 1?

It is shown why Pd/D calorimetry holds the answer, and why the answer to both questions is probably "yes."

Introduction

By now electrochemical Pd/D calorimetry has greatly advanced, both experimentally and in method of analysis. In fact, key data sets from the past, if carefully documented, can be re-analyzed with much enhanced insight. This is very important, especially for the experiments which have come to determine national and international policy.

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Question #2: Are there any Pd/D calorimetric data sets extant which are competent to clearly answer Question 1?

There are indeed experiments which taken at face value do answer Question 1, with a resounding "yes." However, because of the extreme significance of such an answer and the apparent difficulty in nailing down all the parameters necessary to make the experiments repeatable, it may be reasonable to expect scientists to be highly skeptical and require unusually high standards of proof. Also, nature seems to have dealt us a case more profound and evasive than imagined at first. But this should not be blamed on F/P or other researchers. The challenge to science is to solve the case, with hard work and rational dialogue. We shouldn't allow such a smoke screen to be thrown up that the answers can't be recognized even when they are found. We also must be careful that our motives are purely scientific.

To make our position clear at this point we offer two examples from a long list. Mike McKubre¹ et al, using closed cell electrochemical calorimetry both simple and accurate, found and confirmed several times large amounts of excess heat. In their examples the largest total excess heat was 450 eV/atom normalized to the Pd lattice or to the D in the lattice at a loading taken as ~ 1 .

In a completely independent set of experiments, Edmund Storms² found excess heat produced to about 400 eV/Pd atom, in a different closed electrochemical calorimeter design. Before going to other details, stop and focus on the implications of these numbers. Those implications are profound and unavoidable! They must be faced by anyone interested in knowing the answer to Question #1. Consider that the typical heat of formation of chemical compounds, say H₂O, is 1 eV/atom. For an exceptionally stable compound like Al₂O₃ it is about 3 eV/atom. The maximum enthalpy you could store in a Pd lattice by work hardening or any other distortion is about 0.2 eV/atom, the heat of melting. Thus

the excess heat that has been produced is hundreds of times that conceivable from chemistry or metallurgy as we know it.

This enormous excess heat production is the Fleischmann/Pons Effect, FPE. The signature of the FPE is excess heat, and up to now the only practical way of answering Question #1 is by Pd/D calorimetry. That makes the subject interesting indeed

There are other examples of experiments which answer Question #1 with a clear "yes"^{3,4,5,6,7,8,9}. The two data sets that have been most used in deciding if the Fleischmann/Pons Effect, FPE, really exists are the sets of F/P³ themselves and those of Harwell¹⁰. The F/P data sets are the very basis of the FPE in the first place. The Harwell data have been and are (correctly or not) used to argue that there is no FPE. In the hope of clarifying the situation by giving an independent careful evaluation of both calorimetric investigations we have re-analyzed F/P and Harwell data. We have been given a few sets of F/P raw data and all of the Harwell calorimetric data. While the results will be published in much greater detail elsewhere, we make some points regarding the work here. Having the advantage of later and improved analysis techniques, we hoped to discover more detailed information and to improve the accuracy with which the results could be given. Perhaps at higher accuracy we might even find excess heat where it hadn't been realized before or simply agree or disagree with previous analyses, where they existed. In any case, both data sets would be looked at from an independent and different point of view.

Below we report some of our findings using our own analysis of these key calorimetric investigations. We also discuss the implications of these findings.

Some Analytical Details and Implications

General Comments

We submit as self-evident that in these matters experimental observation must always have the last word. And indeed it will. Since nothing involving human reasoning is absolute, it is a matter of individual opinion as to when "yes" is proven by observation. Proving the answer to be "no" is a much more difficult subject. An observation that simply fails to answer "yes" (call it "negative") does not answer "no." It simply gives no answer at all. Failing to catch a fish from a favorite trout stream on a particular outing says essentially nothing about the total absence of fish in the stream. All active researchers doing calorimetry have negative results, and that will probably continue until details are worked out. It is absurd to suggest that Question 1 be answered by taking a tally of the number of positive and negative results. Yet simple negative results have been taken as convincing evidence that the F/P effect does not exist. And current patent and funding policies are driven by a few negative results. Therefore it is extremely important that calorimetric results be examined closely.

We reexamined some of the F/P raw data taken by them and loaned to us¹¹. We have also examined the performance of duplicates of the F/P silvered cells. We had these cells made to the original specs by the same company that made them for F/P. The purpose of this endeavor was to independently evaluate the F/P data and cells by our own analytic techniques. The importance of clarifying the validity of the F/P results would be hard to overstate.

We also obtained the raw data of the Harwell electrochemical experiments, as well as the notebooks. These data were examined to increase, if possible, the information obtained from their analysis¹². We present some of our findings below. This work is not yet completely

finished

Hopefully we have also advanced the state-of-the-art in this type of calorimetry. For example, we show that the F/P silvered cells can be accurate as high as 90°C or so. We examine the question of blackbody radiation in the cell system. We examine the matter of temperature uniformity within the F/P cells, which was such a debated point early on, and actually measure the fraction of the heat flux that actually goes out the top of typical F/P cells. We also use new statistical procedures in attempts to maximize the information extraction from the data. Some of these data have been taken by us using our own F/P type cells.

Numerical examples of F/P and Harwell results

In keeping with the purpose of this short paper to discuss the validity of F/P type calorimetry in an overall sense, two examples of real data sets will be examined, i.e. an example of F/P silvered cell raw data and raw data from a Harwell run. The data are original and used by permission from F/P and Harwell. The emphasis here in this paper is not to investigate excess heat claims, but to demonstrate our analysis of real data. Both the consistency of the data set and the appropriateness of our method of analysis are being tested.

First consider an F/P data set that is run in the usual way but with a Pt cathode giving no excess heat. There are no heat pulses at all for calibration, yet we shall see that our methods still analyze the data very well. The temperature and voltage of the cell are shown in Fig. 1. In the first part of the analysis we took the excess heat as small (the exact value doesn't matter for now) and the cell mass as 5.3 moles water equivalent. We then calculated Kc assuming $K_r = 5.5 \text{ E-}10$. Since the model fails at water refills and when the temperature gets too high, a few computed Kc values will be bad at these times. The bad points are obvious. These outlier points are removed. A linear regression analysis is then run with the cleaned up data set to determine excess heat, heat conduction constant and moles of water equivalent heat capacity (Qf, Kc, and M) simultaneously over the whole data set. K_r is fixed at $5.5 \text{ E-}10$. Each quantity is obtained as a single number which is an average. The Qf is indeed found to be zero within less than 20 milliwatts, and Kc and M are physically reasonable. In fact, we calculated Qf, Kc and M for fifty different regions, obtained from time zero to fifty different times 100 minutes apart from 10,000 minutes to the very end of the data set. IQ_{fmin} was near zero and IQ_{fmax} was $3.8 \text{ E-}02$ watt. The mean Qf was $-1.2 \text{ E-}02$ watt. These numbers indicate the systematic error because we already know the real answer is zero. Relating the accuracy to the 5 watt input to this cell, the mean deviation from zero is -0.24% of the power. We do not take this value as the final calculated Qf, however, because we wish to see excess power as a function of time. Kc is then recalculated at every point with Qf and M held fixed. The result is plotted in Fig. 2. This is the real Kc of the cell as a function of time at all points where Qf is essentially zero, which is everywhere for this cell. The sawtooth variation is due to the daily change in electrolyte level. But the daily average of Kc is nearly constant $Kc \times \Delta T$ is about 9% of the heat transfer due to both radiation and conduction. In Fig. 3 is shown the calculated excess heat assuming a fixed average Kc. We call it oneKcQ to avoid confusion with Qf. The sawtooth variation here is not real, but shows up this way because of the Kc variation. Now the oneKcQ sawtooth variation could be modeled and thereby nearly eliminated, but it isn't worth the effort. The standard deviation, std, for the Qf data set is only 20 milliwatts including the sawtooth variations, and systematic uncertainties that can't be eliminated are about that same amount. Note that the average total input power for this run is roughly 4-5 watts. Also, as we shall see with the next set

of data, when there is a deviation such as a heat pulse, it stands out superimposed on the sawtooth shape and is easily seen. So we see that we can analyze the data to better than 0.5-1% of input power and can see odd pulses to even higher sensitivity, depending on where they show up.

By a similar procedure, but somewhat different, we have analyzed the Harwell data. Here the cell has a Pd cathode in D₂O + LiOD, and it is designed to produce heat to test for the F/P effect. There are also many heater pulses and electrolytic current pulses. In Fig. 4 where we show our determination of $\text{oneKcQ} + H$ (H is the power of an imposed heater pulse), the actual heater pulses are included on the baseline for reference. Note that H is included as an unknown in the analysis so as to see how well we do. Since the heat pulse calibrations were made with a full cell, the zero baseline should go through the oneKcQ curve at a time when the cell is full. Positive deviation along the typical slope until refill is due entirely to change in Kc due to lowering electrolyte level. It appears that the data are unreliable from about 7000 to about 18000 minutes. In the Harwell notebooks a "faulty power supply" is mentioned at this time. Thus the reason for the big dip near the beginning is due to cell malfunction. Even here, however, heater pulses are seen and accurately analyzed, implying that short heat bursts would also be seen. At later times the data are reasonable. Accuracies of about 20 milliwatts (here that is 2%) can be expected in the best regions but this degrades to 60 milliwatts or even 100 milliwatts in other regions (see pulse 8 for example). Total heat power is about 1 watt here, so that ± 20 milliwatts corresponds to $\pm 2\%$.

Results of studies of some key calorimetric problems

First consider the problem of temperature uniformity within the F/P silvered cells. Actually our studies were within our own copies of the silvered cells, made into our own calorimeters. At an electrolysis current of 0.4 amps temperature differences were measured at various pairs of locations with vertical and horizontal separations with a difference thermocouple. In summary, differences of two or three hundredths of a degree were typical. During a heater pulse of 0.3 watt, a bias of up to 0.1 degree was found across the cell from heater to thermometer. Further, a 0.1 degree error was found to change the calculated excess heat, Q_f , by 0.016 watt when a 0.3 watt heat pulse was involved at a 3 watt heat transfer output power or an error of about 1/2%. Actually the maximum observed error would be more like 1/4% because the effective cell temperature was probably close to the mean of the two extremes, making the error itself only about 0.05 degree. These temperature differences, while larger than the reported 0.01 degree, are not a serious problem in our F/P type silvered cells.

There are two types of heat transfer out of the cells besides that due to mass flow. Most of the heat transfer is by radiation. Recall that radiation power is $K_r \times (T_{\text{cell}}^4 - T_{\text{bath}}^4)$ and heat conduction power is $K_c \times (T_{\text{cell}} - T_{\text{room}})$. For one of our typical cells, we have measured K_r at $6.0 \text{ E-}10$ with $K_c = 0.0055$. Given our measured values for K_r , K_c , T_{cell} , T_{bath} , and T_{room} , we compute that 6.9% of the heat is out the top. That means the heat conduction through the top of the cell is about 6.9% of the total heat transfer. Most of that conduction is due to the glass with silver coating plus the wires. In our case we use a plastic foam stopper instead of the Kel-F stopper used by F/P, and the wires are at a practical minimum in thermal and electrical conductivity, and the K_c out the top was measured by fitting an environment controlling hood over the top part of the cell and controlling its temperature separately.

Another important point that needs to be cleared up is the often heard suggestion that several

cells in a water bath may be "talking" to each other radiatively because they are transparent. It has also been suggested that hot spots on the cathode might be seen by an infrared thermogram. We have examined these possibilities quantitatively. We have calculated blackbody curves up to 600°K. We have also measured the transmittance of laboratory pyrex, light water, and heavy water. The results show clearly that the cell electrolyte, pyrex walls, and water bath are all opaque to the calculated thermal radiation. Details are given elsewhere¹¹. Of course if there are hot spots so hot that they have appreciable radiation in the near infrared or the visible they could be seen. But this would require a temperature considerably higher than 600°K.

Time constant effects are important in calorimetry. The radiative heat transfer has the advantage that only the glass walls are involved so long as the contents are "well stirred."¹¹ Experience shows that the typical time constant from this point of view is only a few minutes at most. This gives a great advantage to this type of calorimetry because it is so responsive. By the way, the water bath must also be well stirred to prevent temperature gradients at the cell surface. Conduction out the top of the cell is another matter. It can have a long time constant. However, since K_c is only ca. 7% of the $K_r + K_c$ transfer, a larger error in the process can be tolerated. In fact, if a simple temperature controlled hood is used on the upper half of the silvered top and the hood kept close to the cell temp, say within 3 degrees for a 30 degree ($T_{cell} - T_{bath}$), the effect of conduction out the top is reduced by another order of magnitude to 0.7% which is essentially negligible.

A final effect which we discuss here is that of atmospheric pressure for these open cells. The cells are versatile in that they can be used at widely varying temperatures, even approaching 90°C. At the higher temperature evaporation is an important factor, and depends on atmospheric pressure and equilibrium mixing. We have found that our modeling equations work well to 90°C, as shown in the F/P cell data given below, but the atmospheric pressure need have only modest accuracy at low temperatures (say <50°C) but must be known to about 5% at 75°C.

Conclusions

After a great deal of experience working with F/P data, modeling the calorimeters, and physically using electrochemical calorimeters like the F/P silvered cells, we have found that they are easily capable of 1% accuracy when care is taken and all experimental details are available for the analysis. They can be used to 90°C. Temperature uniformity is adequate, and intercell radiation is not a problem. The cells are rather inexpensive and versatile. All this is a variance with the common wisdom of 1989. Our analysis methods take no shortcuts but can be run in minutes on a workstation once programmed.

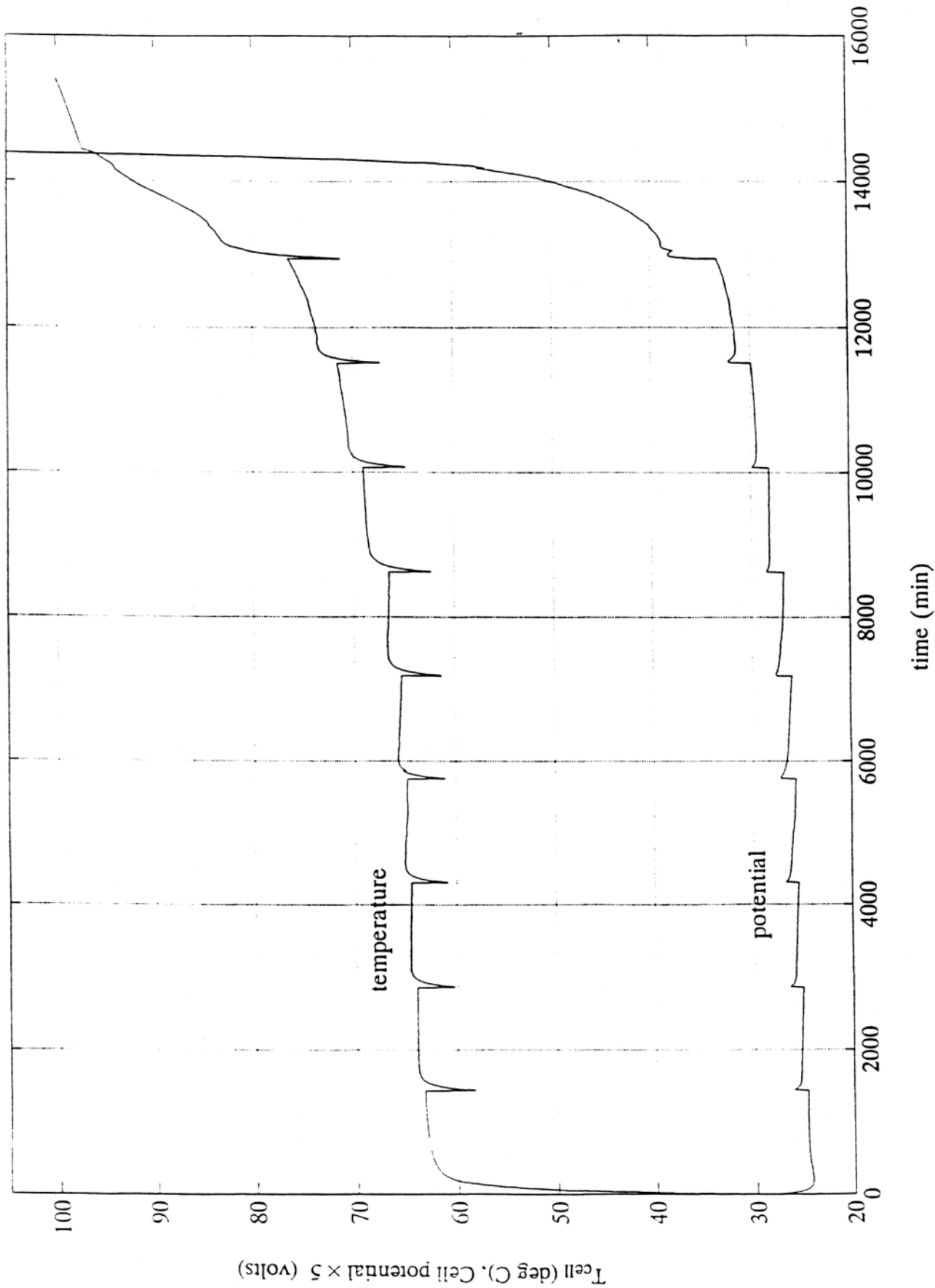
We have applied these analysis techniques to the Harwell FPH electrolytic calorimetry cells. The Harwell FPH cells are not as accurate as the F/P type cells, but over considerable time segments of their operation their accuracy can be reliably characterized. The accuracy bounds that we have estimated are about 2-3% of input power, which is a tighter estimate than derived using Harwell's analysis techniques. We have also determined that the detection of heat pulses above a certain size can be accomplished with the Harwell FPH cells. There are instances, as we reported at ICCF3 in Nagoya in October 1992, where such excess heat pulses are seen. Analysis is continuing of these cells to determine the total excess energy represented by these observed heat pulses.

The excess heat found in the Harwell FPH cells, as we currently understand it, is not definitive with respect to the Fleischmann/Pons Effect, FPE. On the other hand, the Harwell results in no way disprove the FPE. With the luxury of hindsight we now see that Harwell would not have been expected to produce significant excess heat in almost all of their cells because of low current densities, low levels of D loading into the Pd, and other choices in their experimental design. Scientists have no business using the Harwell data as a "no" answer to Question 1!

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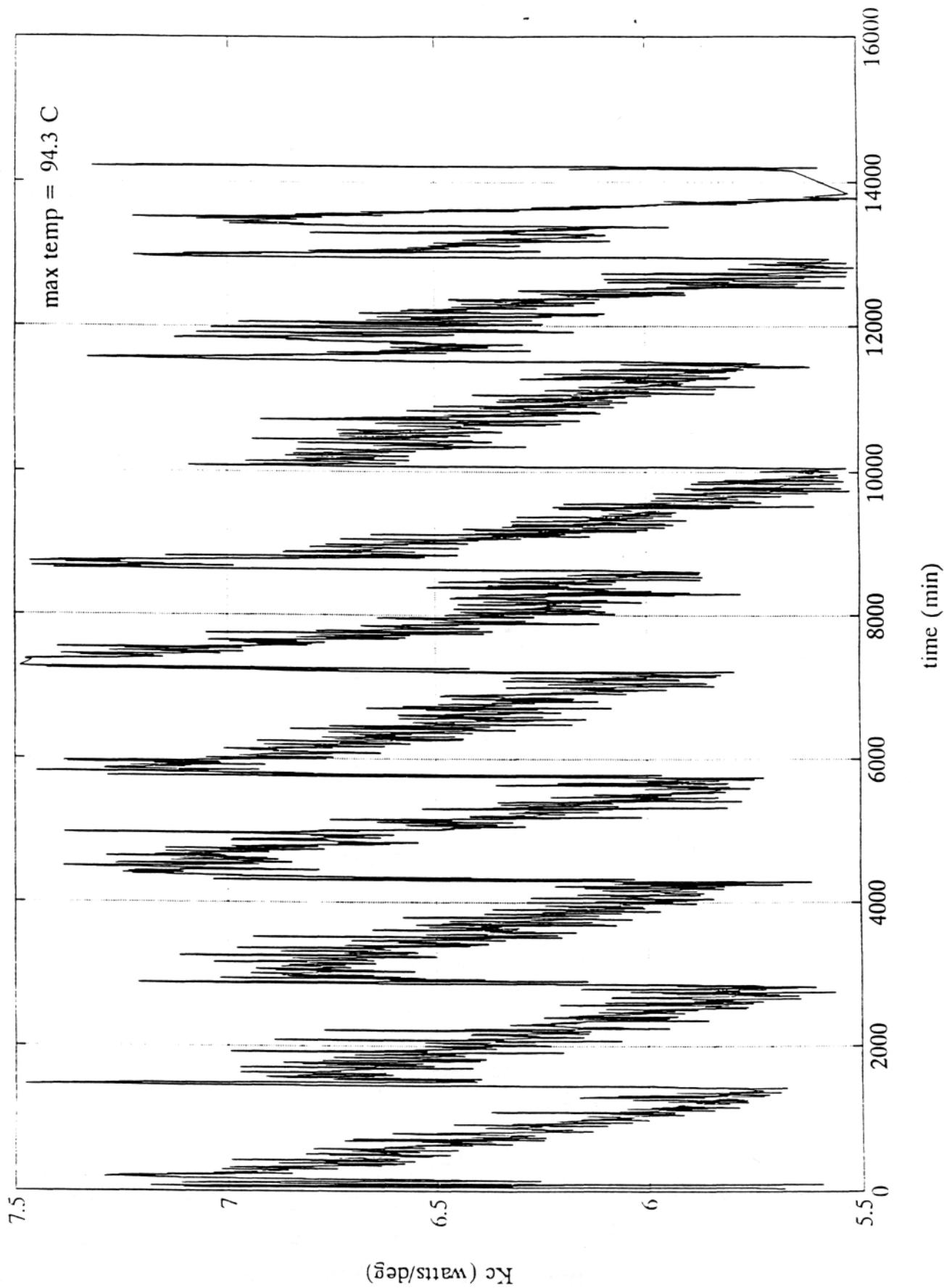
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P/F Cell 1

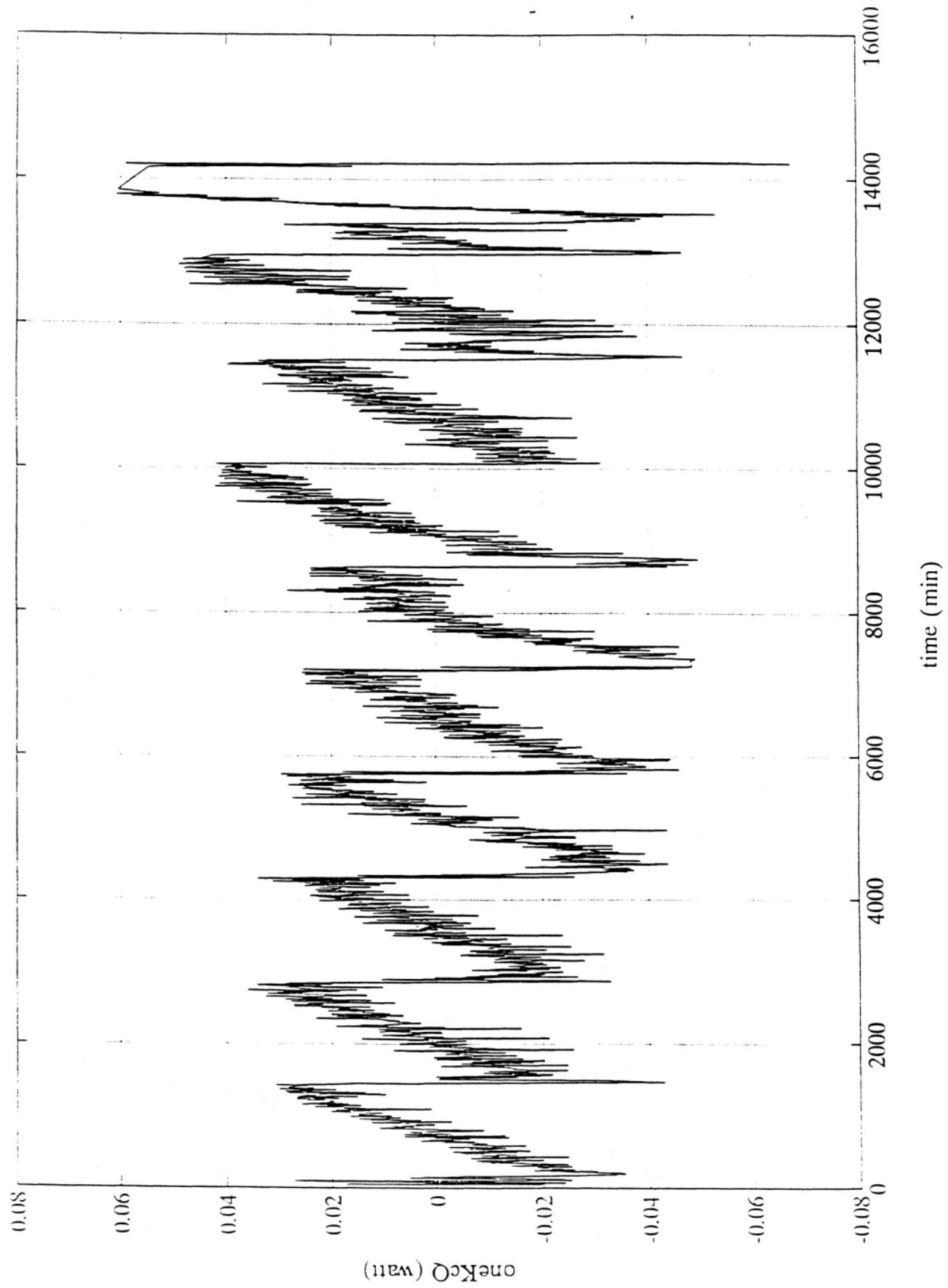


Kc for F/P cell with outliers removed

$\times 10^{-3}$



Excess heat of F/P cell calculated with $K_c = 0.0064$



Harwell Cell

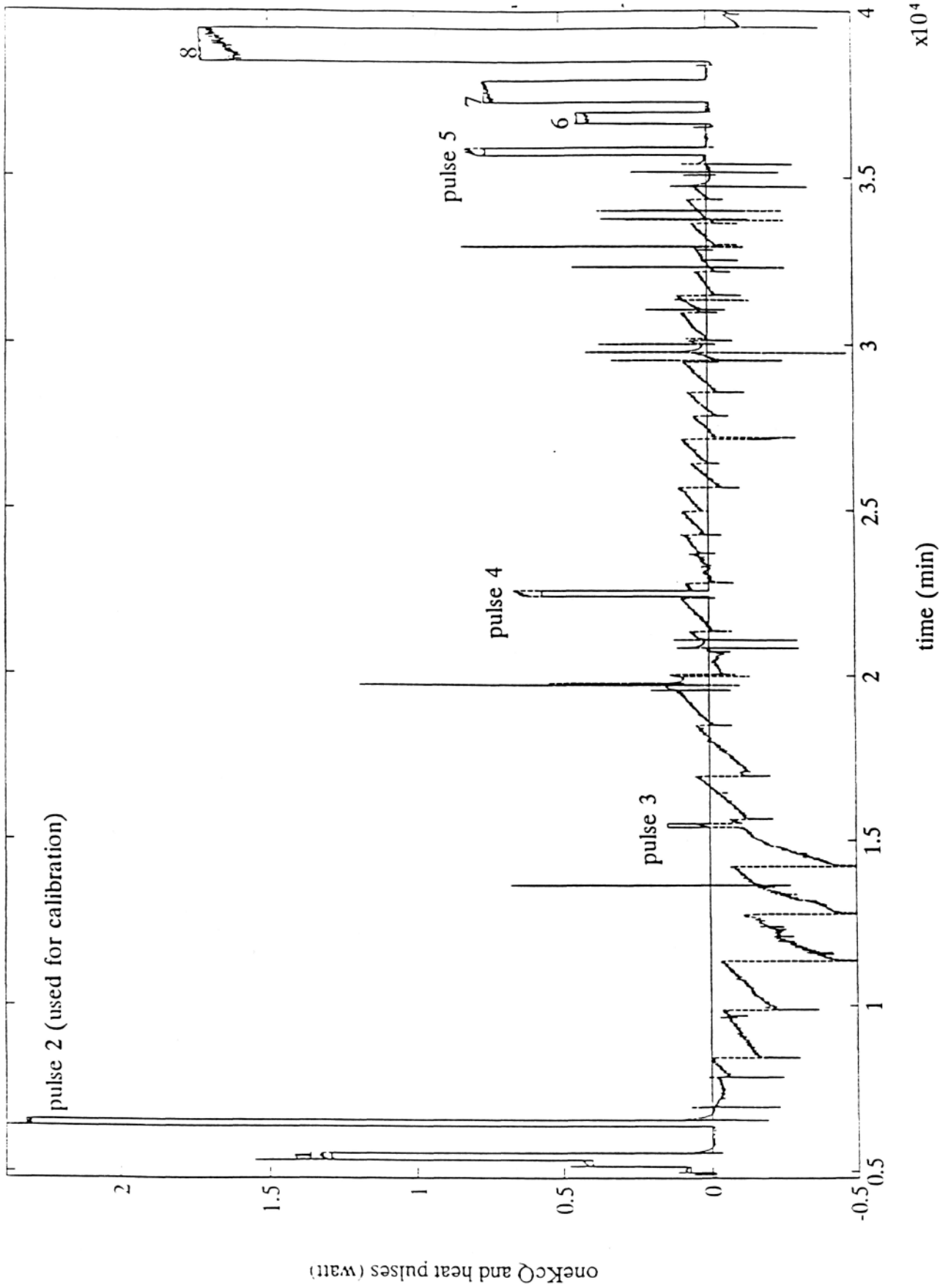


FIGURE CAPTIONS

Fig. 1. Raw temperature and potential of F/P Cell. Current was a constant 0.8 amp.

Fig. 2. Kc of F/P Cell. (Kr is a constant 5.5 E-10.)

Fig. 3. Calculated excess heat using fixed Kc. Variation is due to water level changes.

Fig. 4. OneKcQ of Harwell cell for all points, treating HP pulses as unknown Qf to test the analysis and the performance of the calorimeter under widely variant conditions.