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REPORT TO THE UTAH STATE FUSION/ENERGY COUNCIL ON THE ANALYSIS OF SELECTED PONS FLEISCHMANN CALORIMETRIC DATA

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INTRODUCTION

Here is reported my analysis of a series of electrochemical experiments run by Pons and Fleischmann, P/F. This series produced some remarkable results which were revealed only through a careful analysis.

When I was asked last January by the Fusion/Energy Council of the state of Utah to head a committee to investigate unpublished and unreleased data of Pons and Fleischmann, I knew it would be a difficult and interesting assignment. Still there were many surprises, and it took longer and was more difficult than expected. I received help and good advice from colleagues, including some who were pro and some who were con. While others have helped, I take the full responsibility for this report. I am sorry to say that we have not conducted any actual experiments. In spite of good intentions, the Pons lab has not been used so far in our work. But we have received sets of data and have analyzed some of them in depth. Our strategy has been to obtain and closely examine the most significant data available. We believe that has been done. The data discussed in this report lay no claim to being typical. They are chosen because they illustrate some remarkable results we found to have been obtained by the P/F group.

In approaching this analysis there are many attitudes one could take. Let me illustrate by mentioning three. First consider what I will call “scientific chauvinism.” I have used it myself on occasion. When the University asks me to check out an invention of someone and I find that it is another perpetual motion machine, I just discount it completely and try to get the guy out of the office as smoothly as possible. Some seem to regard the P/F effect in a similar light. After examining P/F data, one “official” reviewer said to me, “They may have something interesting going on, but it certainly has nothing to do with nuclear physics.” A second attitude is one of extreme skepticism. Because of the importance and unprecedented nature of the claimed discovery, and the lack of quick confirmation by most in a worldwide effort, many aren’t going to believe until it is proven beyond doubt. A problem then arises because nothing can be proven “absolutely.” Still something of such profound importance must be given careful scrutiny. A third attitude is that taken by the typical reviewer of articles for, say, Physical Review. He looks for quality in the research, for internal consistency, and for clear results. He doesn’t usually ask to inspect the author’s laboratory, nor does he doubt the word of a scientist with a good reputation. On the other hand even the best of scientists can make mistakes, so careful review is needed, and is usually desired by all.

So what is my attitude in the present case? Well, I have some sympathy for all three cases above. They may all be honest and legitimate attitudes. I avoid the first two because in the present case they would be fruitless. I choose the last, but with more skepticism than usual. The raw data are assumed to be real as given. It would be pointless to do otherwise. But I want to be extra careful on this one because of its great importance. I came into this assignment neither for nor against. Halfway through I was still neutral. I must admit to having become somewhat pro recently, but am trying to remain objective.

OVERALL REMARKS ON THE P/F CALORIMETRY

Neither time on this analysis nor detailed experience with the P/F project are sufficient to allow me to give an exhaustive appraisal.

However critical issues will be faced and evaluated. The most important ones are discussed below.

Adequacy of the experimental setup

The P/F calorimetry has been the subject of a great deal of discussion since March 1989, much of which I have heard. To some extent it's a matter of picking your experts. I make several observations:

1. Improvements have gradually been made to perfect the P/F calorimeters, and the ones used in this series are of the advanced silvered type. This improves constancy of heat transfer and makes analysis easier. It also reduces the heat loss rate by conduction at the top, making the cell contents more uniform in temperature.
2. The assumption of isothermal cell interior has been checked by P/F and collaborators and has been found to be adequate. This has been discussed with P/F and with others who have made independent evaluations. Only one temperature measuring unit was present within a cell in a typical run, however, so consistency of temperature was not continuously monitored. Details of the water bath and other cell environment factors have been reviewed and personally observed and are considered adequate.
3. Loss of electrolyte due to open cell evaporation: according to P/F this has repeatedly been checked with the following conclusions. There is no recombination of electrolysis products inside the cell and the loss rate is approximately as predicted by the mathematical model. Keep in mind that the cells are filled to the mark periodically, typically once a day. A record is kept of how much solvent this takes. Unfortunately these detailed data were usually not available to us. We assume that the cell was full at the beginning after each refill. Observations on blankcells and heatcells tend to show in general that recombination was not a factor. Others who are doing P/F type calorimetry state that with care in covering metal parts above the electrolyte, there is no recombination.

4. It is generally assumed that the voltage, galvanostat, temperature and other instrumental readings had negligible error so far as the instrument itself is concerned, since this is reasonably easy to assure.

Adequacy of the model of the cell calorimetry

This is a subject of active investigation at present and has been the subject of talks and publications in the past. We use the latest P/F model, unabridged, which is well known and will not be given here. There are experts who still say that the P/F model is wrong in certain important respects. This debate will have to run its course as the subject has many subtleties. In the current analysis a competitive model was also used. It made little difference, and made essentially no difference in the crucial aspects of the analysis. It was also observed that the P/F model worked well on the blank cells, even up to high temperatures.

OUR OVERALL APPROACH TO DATA ANALYSIS

Modern fast computers permit the luxury of using the full model equations without approximation. For this reason it is called the “exact” approach. Of course it isn’t really exact. No model of a physical system is exact. But insofar as the model is correct, curve fittings, inversions, and other numerical manipulations can be done in an optimal fashion not limited by trying to make the algebra convenient with the use of approximations. The full blown model equations for open cell calorimetry are rather complicated, and there is little hope of finding simple algebraic solutions. Actually, the latest computers make the use of open cell calorimetry much more attractive. In our approach we avoid many of the arguments about how to reduce the data with approximate methods. In fact much of the criticism of the P/F methods still revolves around how approximations should be made. In our approach, this conflict disappears. For a blankcell, with excess heat known to be zero, it is easy to get the heat transfer coefficients at all times and temperatures within limits which can be determined by digital data analysis. Direct calculations using linear or nonlinear regression analysis can be used to determine both heat transfer coefficient and excess heat in the case of heatcells, Even the effective heat capacity of the cell can be determined at the same time. When heat pulses of known wattage are added to the cell the analysis is particularly straightforward. These can also be used to check the internal self consistency of the data and model. Our data analysis is accomplished entirely with this computer approach.

ANALYSIS OF PONS/FLEISCHMANN CALORIMETRIC DATA

Part One

The cells discussed here are all of the “silvered” type where the vacuum jacket extends out of the water to the top of the cell and the top section is silvered down to a point under the water level of the bath. This makes the heat loss more radiative and smaller. It also makes the change in rate of heat transfer as the water level within the cell goes down during electrolysis less.

The raw data for all cells were received in the form of columns of time and corresponding temperature (Celsius) and cell voltage. The cells were always run in galvanostatic mode, with the constant current given. The voltage and temperatures were recorded every 5 minutes. Auxiliary data for cells 1-5 and cell 8 are given in table 1. The detailed history of the cells was not made available to us, and sometimes there were extraneous data attached before and/or after the run of interest. Nor was the serial number of the flask used given. Because the cells were not all alike, it may prove very useful to have these and other data in the future, and they may be available from notebooks.

First we will discuss the “blankcells”, i.e., cells deliberately designed to be like the “heatcells” but produce zero “excess heat.” For these, $Q_f = 0$, except for small amounts due to loading at the beginning. In this set there are two, cells 8 and 3. Cell 8 is blank because a platinum electrode (three 1 mm dia. x 1.25cm Pt wires bound together) was used instead of palladium. Otherwise the cell contents were the same as those used in the “heatcells”, i.e. those intended for possible heat production. Cell 3 used the same type of cathode as cell 8. In addition light water was used. Cell 1 is claimed to be the same flask, but is a “heatcell”, with heavy water and palladium cathode. There may be other small differences, here and among the cells in general. For example the heat capacities of the various cathodes are probably somewhat different. Also the cells may not all have had the resistance heating well and resistors in place, since heat calibration pulses were not used in cell 8 nor in cell 1 in the main run. Early on it was thought that cell 3 was a blank for cell 7, but that proved not to be the case. From the information we have, cells 1, 3, and 8 are the same flask and all others are different individual flasks with none in common. Cell 3 used a platinum cathode (three 1mm dia. x 1.25 cm Pt wires bound together). Using hindsight, the fact that most of the cells had no blank is of course unfortunate. It would be nice to have blankcells for all heatcells, and to have in addition heat calibration pulses for every cell, including all blankcells. The most important change in this set of similar cells from an analysis point of view, is that the heat transfer coefficients vary from cell to cell.

TABLE 1

Auxiliary Data for Cell Runs

Run	Cathode	Electrolyte	Heat Pulses	Current
Blankcell	Pt wire	D_2O + LiOD	None	800 mA
Cell 8*	3-1 mm x 1 .25 cm bound together	0.1M		
Blankcell	Pt wire	H_2O + LiOH	Two	800 mA
Cell 3*	3-1 mm dia x 1.25 cm	0.1M	0.270 watts	
Heatcell	Pd alloy	D_2O + LiOD	One	800 mA
Cell 1*	4 mm dia x 10 cm	0.1M		
Heatcell	Pd alloy	D_2O + LiOD	One	200 mA
Cell 2	1 mm dia x 1.25 cm	0.1M	0.270 watts	400 mA
Heatcell	Pd alloy	D_2O + LiOD	One	400 mA
Cell 4	4 mm dia x 1.25 cm	0.1M	0.270 watts	800 mA
Heatcell	Pd alloy	D_2O + LiOD	One	400 mA
Cell 5	2 mm dia x 1.25 cm	0.1M	0.270 watts	800 mA

* Cells 1, 3 and 8 are same flask, other cells all have different flasks.

EVALUATION OF BLANKCELLS

Now concentrate on cell 8. The raw data are plotted in figure 1. Further data include: the cathode comprised three platinum wires 1 mm in diameter by 1.25 cm long, wrapped together, the electrolyte was 0.1 M LiOD, and the current was 800 mA throughout. Data for the fillings with D_2O were typically 8.0 ml per day for a cell using 800 mA. The detailed filling data for cell 8 are not given, but the behavior of the raw data indicates that they were regular and uniform. We will now present an analysis scenario that reveals a number of characteristics of this cell, and indicates some general things about this type of cell. We use a real-time Kalman filter and run through the data from left to right (increasing time). This gives us a relatively noise free data line for Q_f as a function of time throughout the whole set of data. The model used to calculate Q_f is that of Pons/Fleischmann, (P/F hereafter). Since the model does not hold for the short time of water refreshment, a spike in the filtered Q_f output results. In addition, the Kalman filter takes a few points to settle down after the spike, so there is a period of time after each refill where the filter output points are first false and then doubtful. These periods are obvious from the graph, figure 2. In running the filter, a fixed radiative heat transfer coefficient, K_r, for the cell is given and Q_f calculated. Actually, of course, Q_f should be zero everywhere if small chemical changes in the platinum electrode are neglected, which appears reasonable. This requires a K_r that changes as the day progresses. The small changes involved seem transparent at this point and will not be plotted here. (We will, however, confirm our results by another approach later.) We take the data for a given day as a batch, use a curve fit to, say, $Q_f = 0$, using an appropriate modelling equation, and see what the average K_r is. K_r may also be taken linear with time or quadratic with time. At this point it should be noted that the heat transfer is not pure radiative but has a conductive component which is given by $K_c(T_{cell} - T_{bath})$ while the radiative heat loss is given by $K_r(T_{cell} - T_{bath}^4)$. Using the current type cell it is nearly correct to use the pure radiative heat loss mode, at least for cells with a coefficient of, say, $6.1\ 10^{-10}$ or less. It should be noted that by using pure K_r and no K_c, Q_f is underestimated and not vice versa. By using both modes and two heat loss coefficients, the blank cell heat loss could be fit at the first and last days without changing the K_r value. The change probably occurs because at high temperatures the use of the power four terms overstates the heat loss a bit. However, the change in K_r is so small in the present case that the use of a pure radiative term is a good approximation. We will return to this point later. At this point let's see what K_r is required to fit cell 8 to about 90°C.

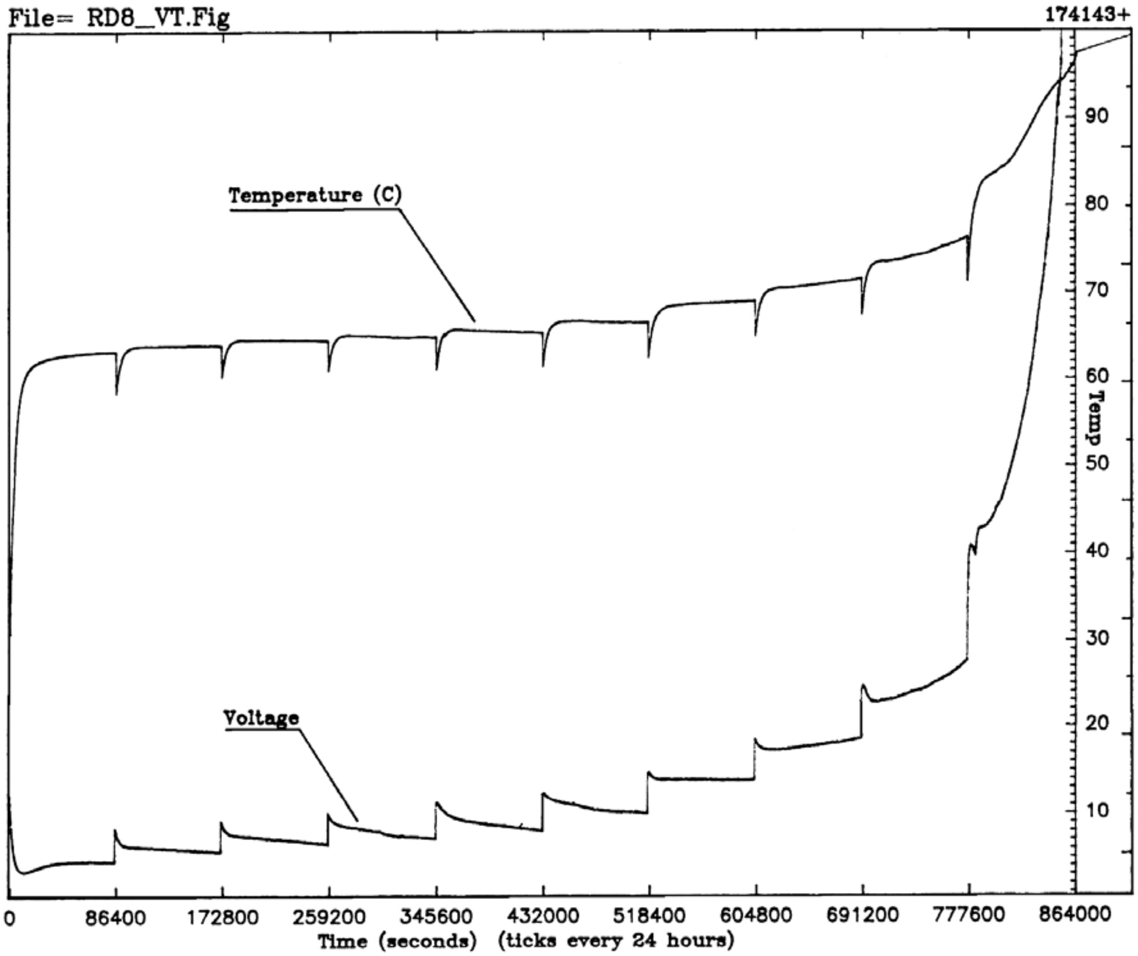

Figure 1. Plot of raw data for blankcell 8 experiment. Electrolyte is 0.1 F Li OD in D_2O. Cathode is Pt.

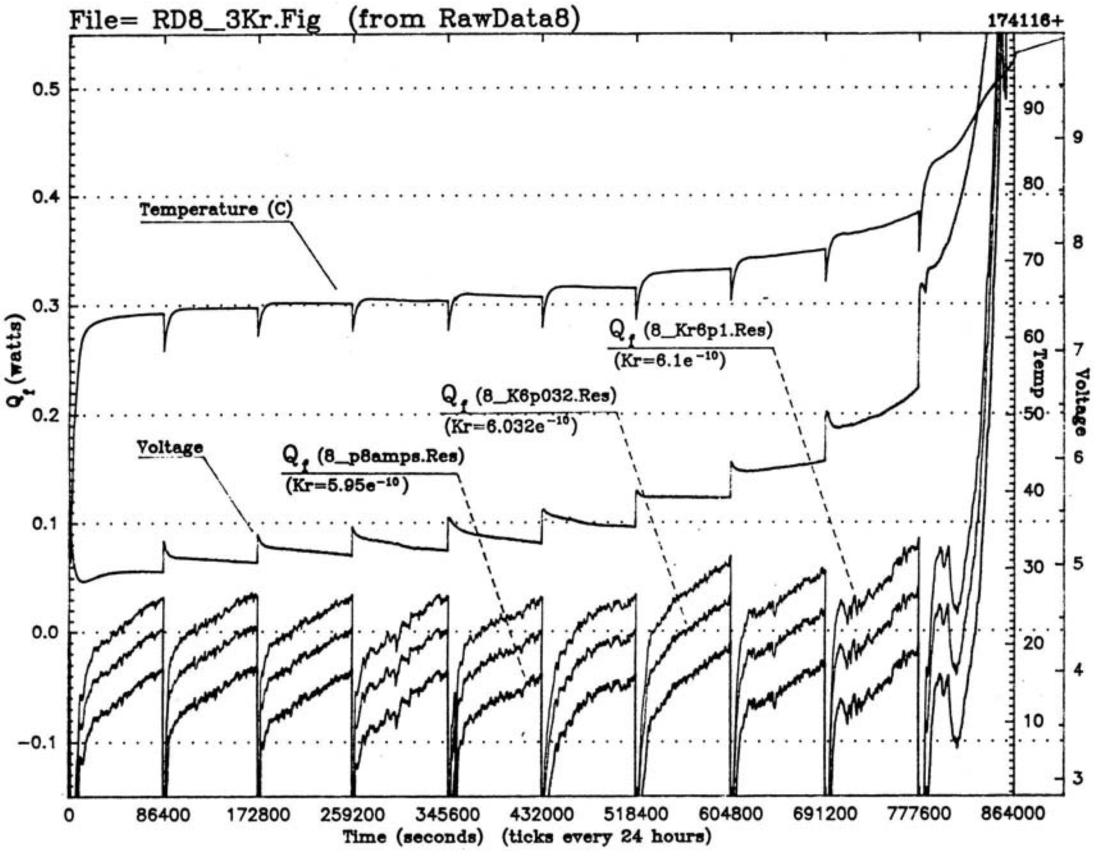

Figure 2. Cell 8 experiment. Kalman filter calculation of Q_f to show what K_r must be for this blankcell.

Because the cell is open and the contents change throughout the day, the actual K_r of the cell changes a little also. The strategy used here is to find the K_r that gives $Q_f = 0$ at the middle of the day. It will be seen from the graph that $K_r = 6.1\ 10^{-10}$ accomplishes this quite well at the beginning of the run. At the end of the run, after the last filling, up to where the temperature approaches 90°C, K_r=6.032 10^{-10} does the job. This is a change of 1.1%, and within the precision we have come to expect in this analysis. The use of K_r=5.95 10^{-10} clearly gives results too low everywhere. We will present other analyses below and look into things in more detail, but we can see right now that the model fits what is happening to +/- 2% or so throughout the entire cell history up to 90°C or so (keeping in mind that the regions associated with the steep spikes downward don't count). All this is very important, for this cell covers the high temperature range where it was thought by some to be too difficult to model the cell properly and take data accurately. The low temperature region is indeed easier to model, especially if it is rather constant in temperature. This is true for two reasons. First the heat balance equation becomes very simple and, second, the K_r remains nearly constant with time. Another point needs to be made here. If a heatcell produces no heat, it is impossible to distinguish it from a blankcell. From the analysis of cell 8 we know what to expect in general from other cells of similar design. We also know some behavioral patterns even of heatcells. For one thing, the model works up to about 90 deg C if temperature and voltage don't change too fast.

Cell 3 will not be discussed in detail at this time. The two heat pulses of this cell were not steady for some reason. It does appear that parts of the heat pulses were proper and assuming that these sections represent the 0.27 watts intended, the K_r value obtained by fitting these sections does indeed give a Q_f of zero, showing internal consistency.

ANALYSIS OF A HEATCELL

Now consider a heatcell set up in the same flask. The only change is that the cathode is now palladium and a little larger which increases the heat capacity a little. (But as we shall see this size is of little importance in the analysis). The raw data are plotted in figure 3 for this run. Note that there is an instrument problem that gives a spurious hump in temperature the last day. Evidently these points can be simply ignored, which we have done, including the short Kalman filter glitch evident in figure 4 where we include the filter output for K_r=6.1 10^{-10} and for 6.032 10^{-10}. The former is for the lower temperatures and the latter for the higher, as indicated by the analysis of cell 8. Of course the cell constant could have changed during runs, but there are no data to point to such a change, and the change might just as probably have given a larger K_r rather than the smaller K_r required here to give a zero Q_f, i.e., make it look like a blankcell. If the K_r remained constant from run to run we could already be certain that there was a modest amount of excess heat produced, increasing with time and temperature, the maximum being about 0.38 watts.

Now let us use a different analysis approach on these two runs in the same cell. Here we will use nonlinear curve fitting, also called nonlinear regression analysis. It is based on minimization of the mean-square error as explained in a handy book by S.M. Bozic pp 92 ff [1], see also refs [2] and [3]. To accomplish this the Marquardt-Levenberg algorithm is used. At first we will simply assume that K_r is a constant for a day, take the day's data points as a batch and find the best K_r that fits the day. We could just as well let K_r vary linearly or even quadratically through the day. The convergence of the iterative process works very well. It is just more cumbersome to discuss, and the single K_r per day is well within a 2% accuracy. Along with the computed values we will be giving data that indicate expected errors in those values and other statistical data.

In a typical day there is only a point or two that cannot be fit by the model. The model does not work for the few minutes it takes to add D_2O to refresh the cell. However uniform temperature should return within the cell within a few minutes, and only a point or two need be lost. (Data are taken every five minutes). Avoiding these points, the rest of the day's points are useable. In the case of the blankcell they are taken as a batch and used to fit the equation Q_f =0. There are differences in the P/F and Walling formulas. These are small at low temperatures. The P/F formulas use more detail which may become important at the high temperatures. We have used both. We have modified the Walling formula to use the full K_r $(T^4-T_b^4)$, and call it MWF.

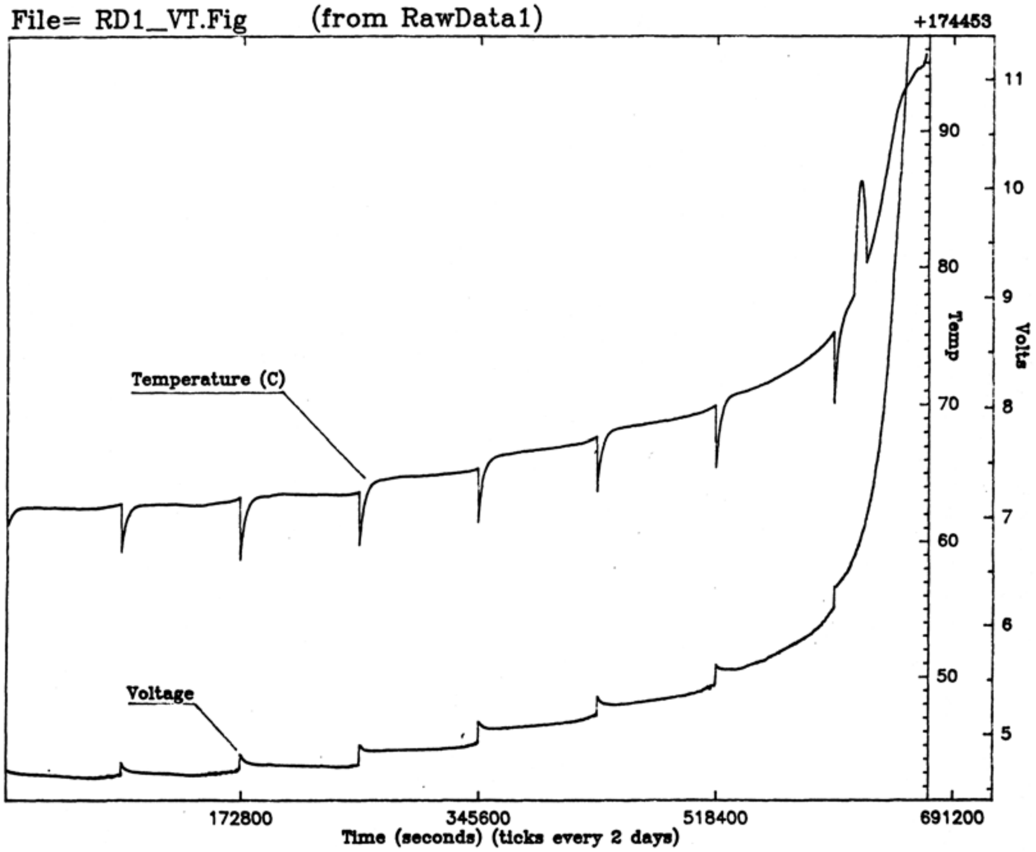

Figure 3. Plot of raw data for heatcell 1 experiment. Electrolyte is 0.1 F LiOD in D_2O. Cathode is Pd.

Heatcell 1 is first analyzed by running a Kalman filter for Q_f over the entire run with K_r set at the values indicated by the blankcell run, i.e., K_r=6.032 10^{-10} and K_r=6.1 10^{-10}. The results are presented in figure 4. A modest excess heat is shown. (Remember that even a small deviation from the blankcell is significant in the sense that it demands an explanation.) Perhaps the excess heat in the present case is just some chemical reaction with the electrode. Perhaps it is simply due to the K_r of the cell changing since the cell was used as cell 8. This isn't expected, but if K_r were smaller during the heatcell run, and the larger expected values were used in the calculation, erroneous excess heat would show. From this point of view it would be nice to know the history of the cell. We don't. Just to show what value of K_r would be required for Q_f=0, we have made the necessary Kalman filter calculation and show it in figure 5. Note that even at this low K_r of 5.63 10^{-10}, there is still excess heat. This is a forced fit, but it shows how important it is to know the cell histories and relationships. Perhaps some mistake has been made in identifying cells, or possibly the cell constant has changed. At the moment we have no way of knowing for sure. We need a better calibration procedure, which we demonstrate below.

ANALYSIS USING HEAT PULSES

Actually P/F have designed at least some of their cells with a resistor placed in a tube near the bottom of the cell, in about the position taken by a small cathode. The idea is that at any time desired they can superimpose a known amount of extra power into the cell. They have done this by putting a fixed and known current through the constant resistance. Occasionally they measure the voltage also to confirm the wattage. This then gives a heat pulse that should give exactly the same results as a transient Q_f of the same shape. If the heat pulse is known, the response of the cell to Q_f is indicated. The heat pulse can be turned on at any time and temperature. These calibrations occur right in the midst of the cell run at just the time the data are needed. In our opinion they are the answer to cell evaluation and they should be used extensively, on blankcells as well as heatcells.

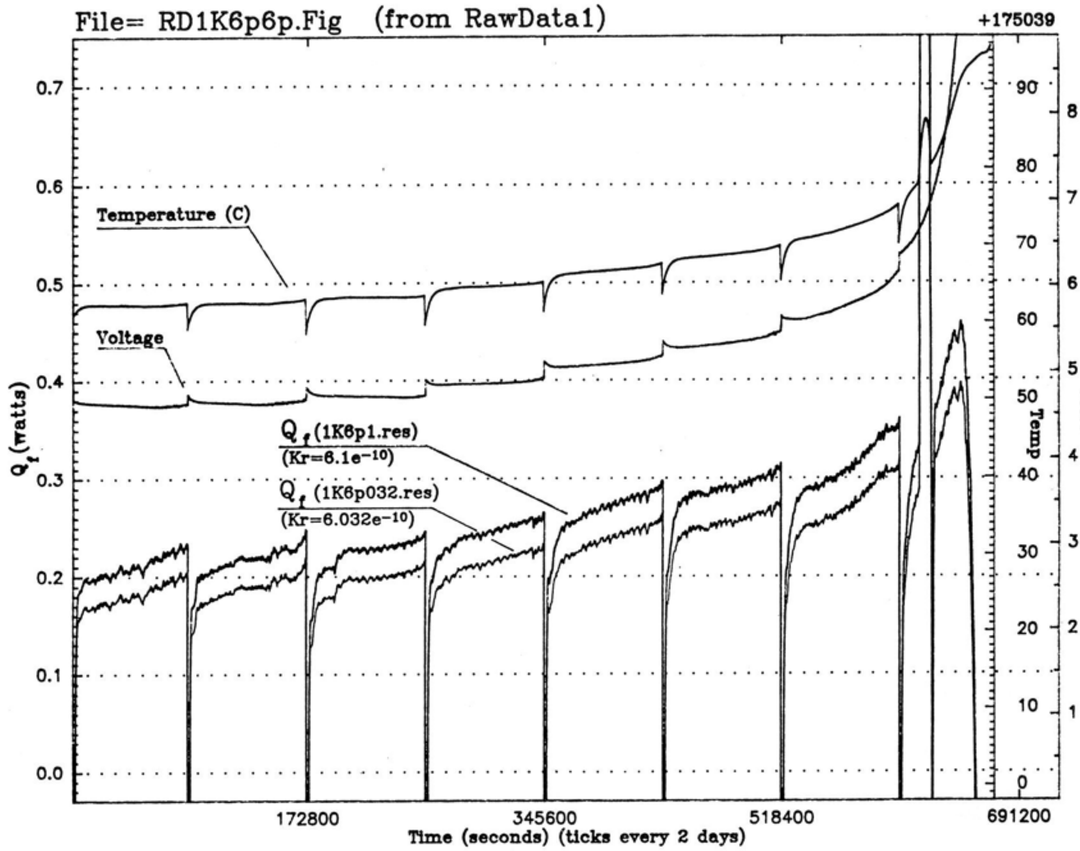

Figure 4. Cell 1 experiment. Kalman filter calculation of excess heat, Q_f, assuming heat transfer coefficients of cell 8, the same flask.

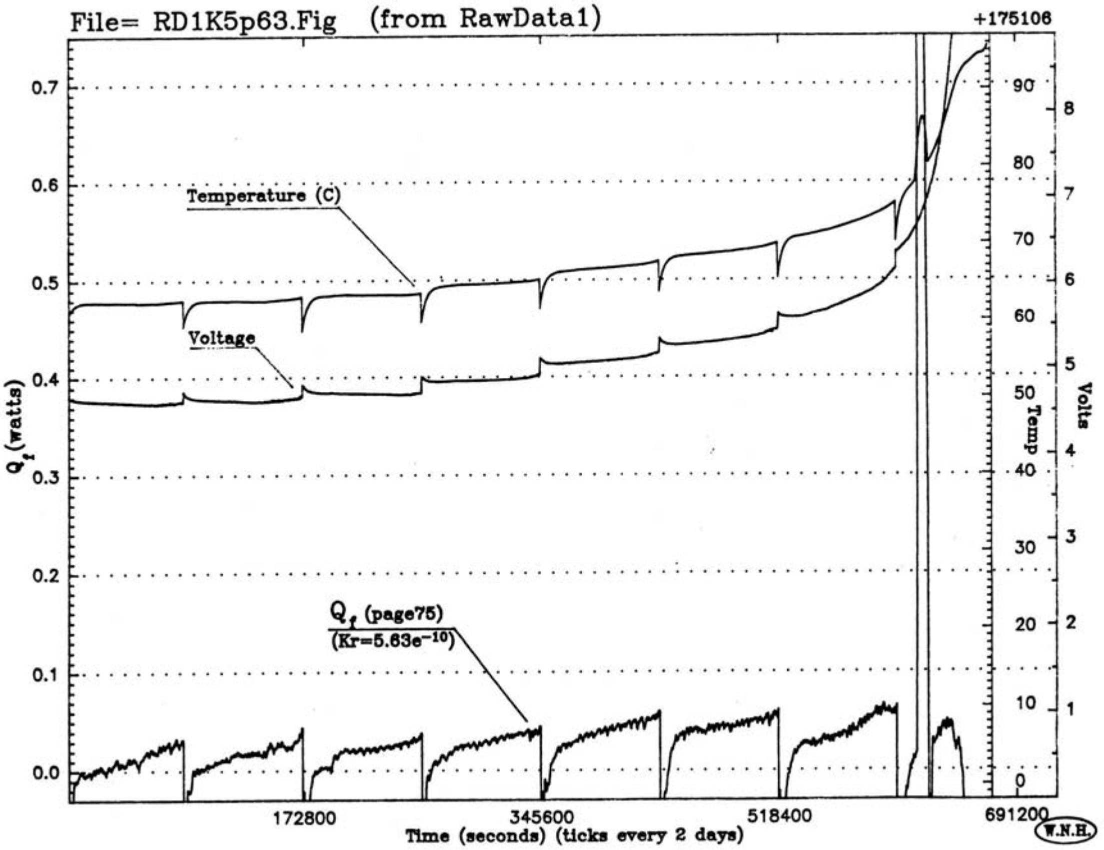

Figure 5. Cell 1 experiment, showing the K_r required for blankcell status and the resulting Kalman filter calculated Q_f.

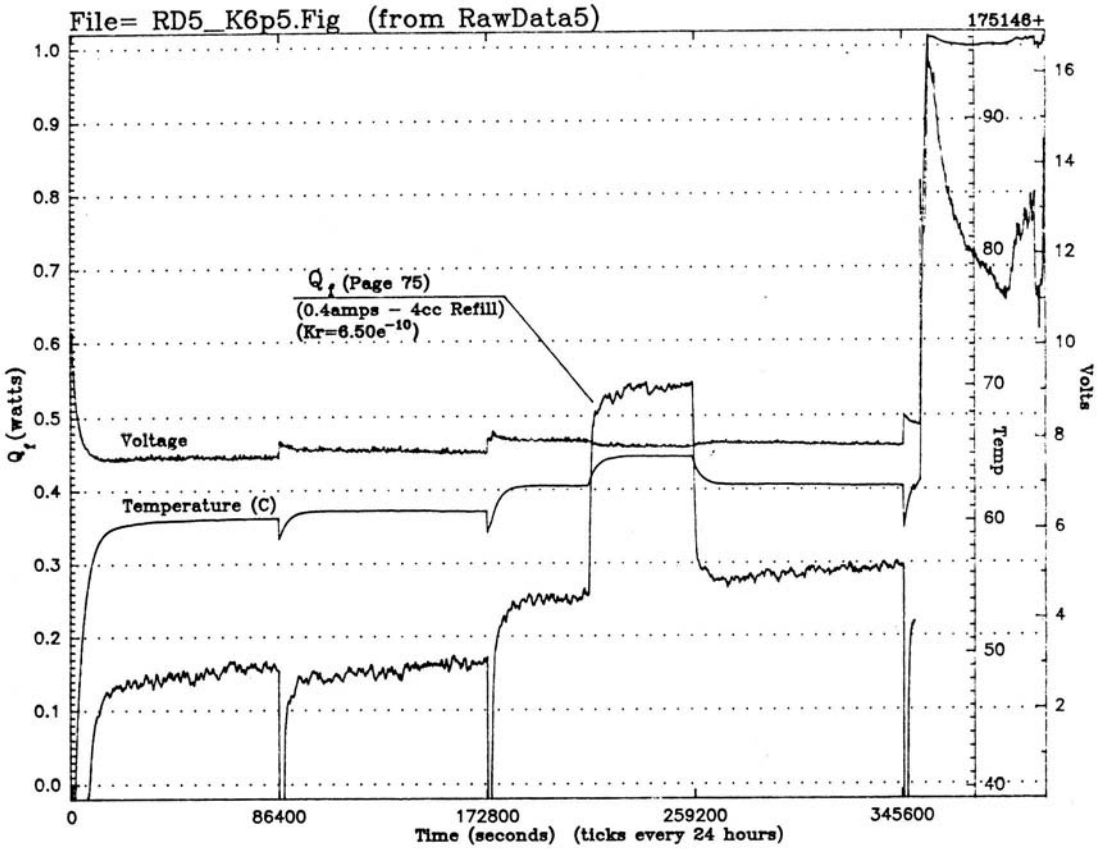

Figure 6. Raw data and Kalman filter output of cell 5 with heat pulse of 0.270 watts. The K_r used is required to make the heat pulse equal to 0.270 watts. Note the sudden increase in Q_f near 172800 seconds, not characteristic of a blankcell. Also note the very rapid temperature rise to boiling at the end.

Before we discuss how we use the heat pulses to analyze cell behavior we mention that they have been the subject of no small controversy. It seems to us that the source of this controversy is the fact that the cell voltage changes during the pulse due to the change in the conductivity of the electrolyte as the temperature changes. This in turn is probably due mainly to the increased mobility of the ions with temperature. There can be no argument if the data are handled by one of the regression methods we discuss below. The results of calculations using the pulses are unambiguous and very accurate. Of course we are thinking of numerical accuracy. The calculations cannot be accurate if the power of the pulse is not known accurately.

We have used the heat pulses in several effective ways. All are in perfect agreement with each other. The method of choice depends on what is wanted. One method is to simply run the Kalman filter for Q_f using a K_r that gives the known correct pulse height. This is easily estimated after viewing the results of a close guess. The height of the pulse can readily be determined by sight, a straight edge and a set of vernier calipers, after the Kalman results have been plotted in large profile. Notice that the Kalman filter treatment reduces the pulse to a step function. It is not necessary to measure the pulse height by hand, however. The full power of batch processing and statistical treatment of data are available in curve fitting. The heater pulse wattage, HP, is known as a function of time, as are other variables. We can solve the needed equation for HP = "..." and fit "..." to the known value of HP. In doing so we allow K_r and Q_f to seek their values, using a nonlinear fit algorithm (actually the algorithm can be a general linear fit, since "linear" refers only to the coefficients allowed to vary). The convergence of the iterations is fast and the answer is sure. In fact C_p can also be allowed to seek its own value, typically with little effect on K_r or Q_f if T isn't changing very fast. In fact at places where the temperature is changing rapidly (but still in equilibrium within the cell), Q_f, K_p and C_p can sometimes be found without a heat pulse present, but with less accuracy. Typically data are treated a day at a time in this curve fitting process. On occasion, however, we have treated multiple days in one session.

As an example of the nonlinear regression analysis consider heatcell 5. The raw data along with a Kalman filter calculation of Q_f are shown in figure 6. Note that K_r is chosen to give a heat pulse of 0.27 watts, the value of HP for this cell. (The value of HP is 0.27 watts for all of the pulses used in this set of cells.) When the data are fit to HP throughout the two day period, K_r=6.5 10^{-10} is obtained with statistics as given in table 2. It is seen that the fit is good and there is no doubt about the excess heat calculation from the data. This of course depends on the data being accurate. A point to mention here is that even if the K_r is obtained by letting the Q_f at the beginning of the run, day 1, be zero (the most conservative situation possible) and ignoring the heat pulse data, there is still excess heat as shown in figure 7.

Cell 5 is claimed by P/F to give a great deal of excess heat at the end. The data and reasoning are as follows. All but a small amount, say 5 cc, of the electrolyte was smoothly boiled away at the last after the current was raised to 0.8 amps, within a period of 42 minutes. The raw temperatures and voltage of this period and beyond are given in figure 8, as well as a marked off 45 min period. The higher current starts at the left of the 45 min period. The liquid was down to the position of the small electrode in the cell within 45 min. Let us perform a quick simple calculation to see what this implies. There was about 3.3 moles of D_2O boiled away in say 45 min. The heat of vaporization at 101.4°C is 496.5 cal/gm or 41550 joules/mole. Take this as the value to use here. This translates to ca. 114 kJ excess heat in 45 min (assuming 9 watt input), or 470% excess heat. The electrode has only 1/226 of a mole of Pd. This gives 267 eV/Pd atom for the excess energy. It also corresponds to about 1 kilowatt per cc of Pd electrode. It only takes about 5 eV per Pd atom to heat Pd to 4000°C and vaporize it. Cell 4 behaved almost exactly like cell 5 throughout a similar run, and the data show that it also boiled off in a similar fashion in the same time period, with the same results. The electrode was four times larger, so the effects per Pd atom are about four times less. This analysis depends on the accuracy of the data given. In the case of the boiloffs the data are somewhat subjective. One would think they could hardly be off by more than, say, 50%, however. If the data are anything like that reported, they are spectacular! Of course we can discount them completely. That is a separate issue. This analysis is conducted as though the data are reasonably reliable. These last data on the spectacular heat production at the last of the run were reproduced on a second cell, for example, which should decrease the chance for misunderstanding or outright mistake. The idea that the fluid was expelled like a geyser was considered, but smooth boiling can be expected from a cell with a constant source of nucleated bubbles at the electrode surface. In addition it was reported by Pons that the boil off was only liquid free vapor.

TABLE 2
Fitting of Cell 5 Data

Fit	Range	Value	% Random error Estimate	Comments
1	entire 2-day period with heat pulse	$K_r = 6.479\ 10^{-10}$ $Q_f = 0.248$	1.0 11.5	C_{po} fixed at 434 modified Walling formula (MWF)
2	entire 2-day period with heat pulse	$K_r = 6.571\ 10^{-10}$ $Q_f = 0.288$ $C_{po} = 472$	1.0 10.2 17.7	C_{po} also allowed to fit MWF

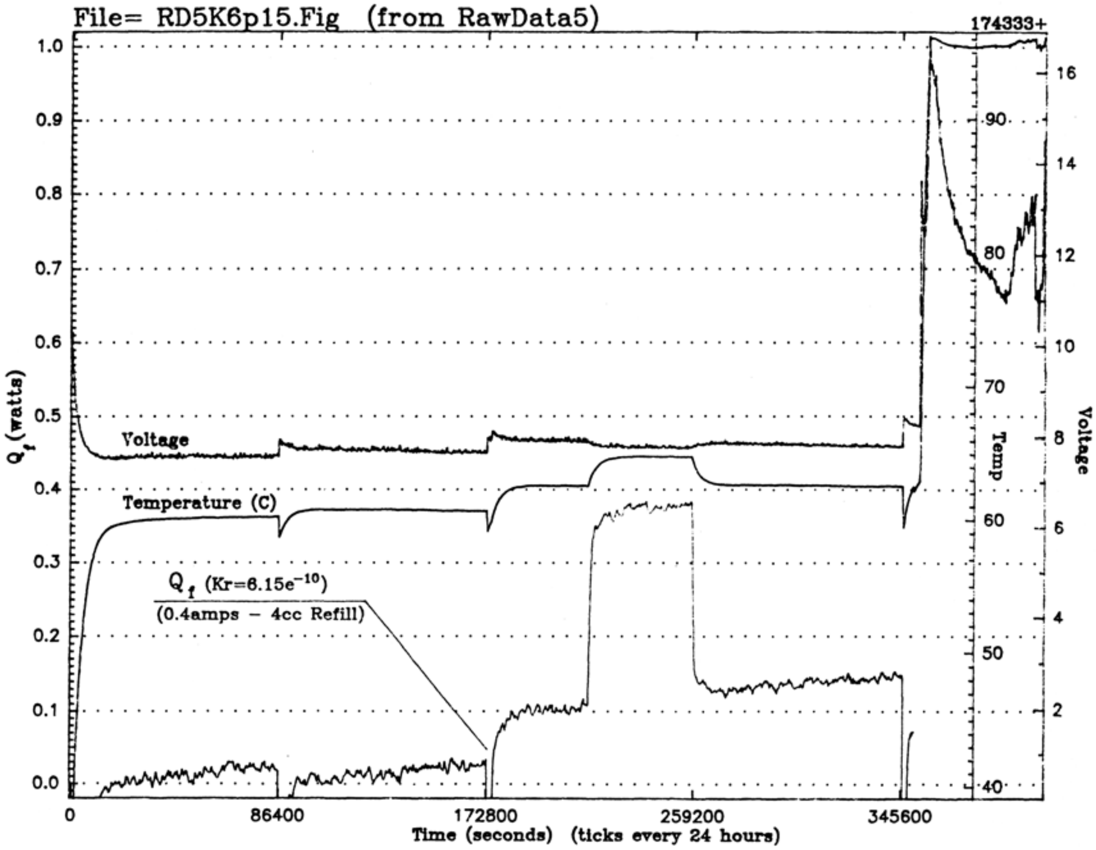

Figure 7. Kalman filter output for cell 5 experiment using a K_r that gives Q_f=0 at the beginning. This gives a lower bound on Q_f for this heatcell, ignoring the heat pulse, and shows that Q_f is still significant at the end of the 0.4 amps period.

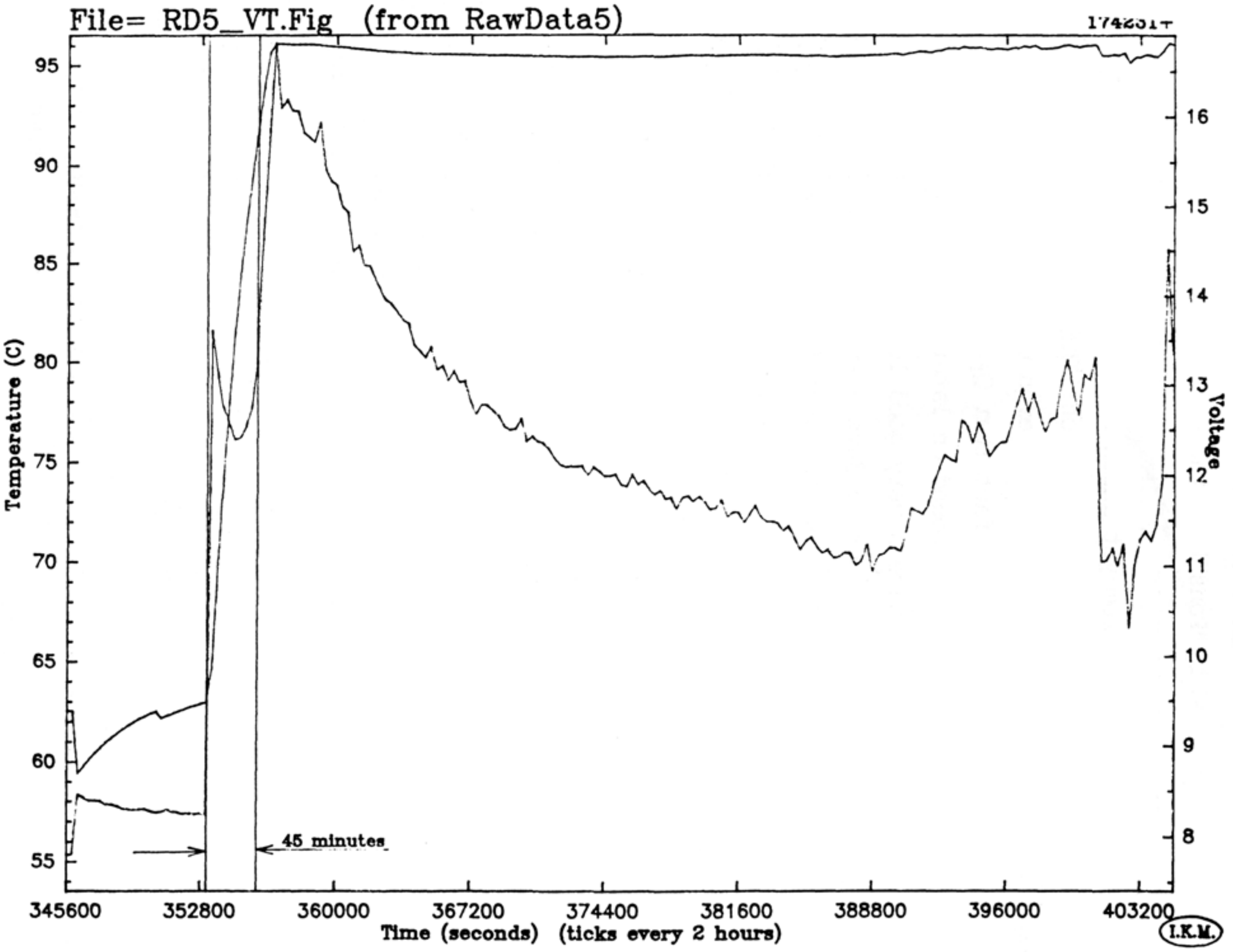

Figure 8. An expanded view of events at the end of the cell 5 run. About 3.3 moles of D_2O were vaporized in about 45 minutes.

Let's look at cell 5 from yet another point of view. The behavior of the cell is ideal in the 0.4 amps region. The model is expected to fit very well indeed. Suppose we don't even use the heat pulse for calibration. We simply use the fact that Q_f isn't expected to be negative in order to get a lower bound on later Q_f. Set $Q_f = 0$ at the beginning of the run. We now have a very good lower bound. Consider the plot of Q_f again in figure 7. During days 3 and 4, Q_f cannot be less than 0.1 watts or so—say 0.11 watts. Just for the two days this corresponds to 45 eV per Pd atom. This is already an order of magnitude larger than the energy to vaporize the entire Pd electrode. We have thought of no other self consistent explanation than that the excess heat is real and very significant. Also notice that the smallest K_r that can be given this cell is $6.15\ 10^{-10}$.

In figure 9 are shown results for cell 4, almost identical to those for cell 5. It will be noticed that here the K_r dictated by the heat pulse is $6.43\ 10^{-10}$, while the value that puts $Q_f = 0$ at the left end is $5.95\ 10^{-10}$. Statements about excess heat are essentially the same as for cell 5 except that in cell 4 there is four times the Pd. Also note the rapid boiloff just as in cell 5, with similar implications with regard to excess heat.

ANALYSIS OF HEATCELL 2

This cell was run at 0.2 amps for a short while, and then increased to 0.4 amps. It took about three days at 0.4 amps to reach 95°C. The first two day period at 0.4 amps contained a heat pulse of the usual 0.27 watts. Solving the model equation for heat pulse power, HP, and then fitting the equation to the known HP as a function of time gives the excess heat, Q_f, and the cell heat constant K_r. Once again, assuming the data are correct as given, there is little room for doubt as to the required values of K_r and Q_f. The statistics for the data are given in table 3. This fitting process is done by the batch method, where the batch of points is taken over a time period where Q_f and K_r change very little. The average values of Q_f and K_r are found. An advantage of the Kalman filter calculation of Q_f is that it gives the dynamic Q_f as a function of time. It does, however, have a several point time constant, say six or eight 300 sec periods. (Points are taken every 300 sec.) Figure 10 shows the raw data of cell 2 plus a Kalman filter calculation of Q_f assuming $K_r = 6.57\ 10^{-10}$, which is required to fit the heat pulse to 0.270 watts. Also included is the calculation of Q_f using the P/F formulas, using the same K_r. This is also about the same K_r as found by the regression approach (see table 3) in the heat pulse region.

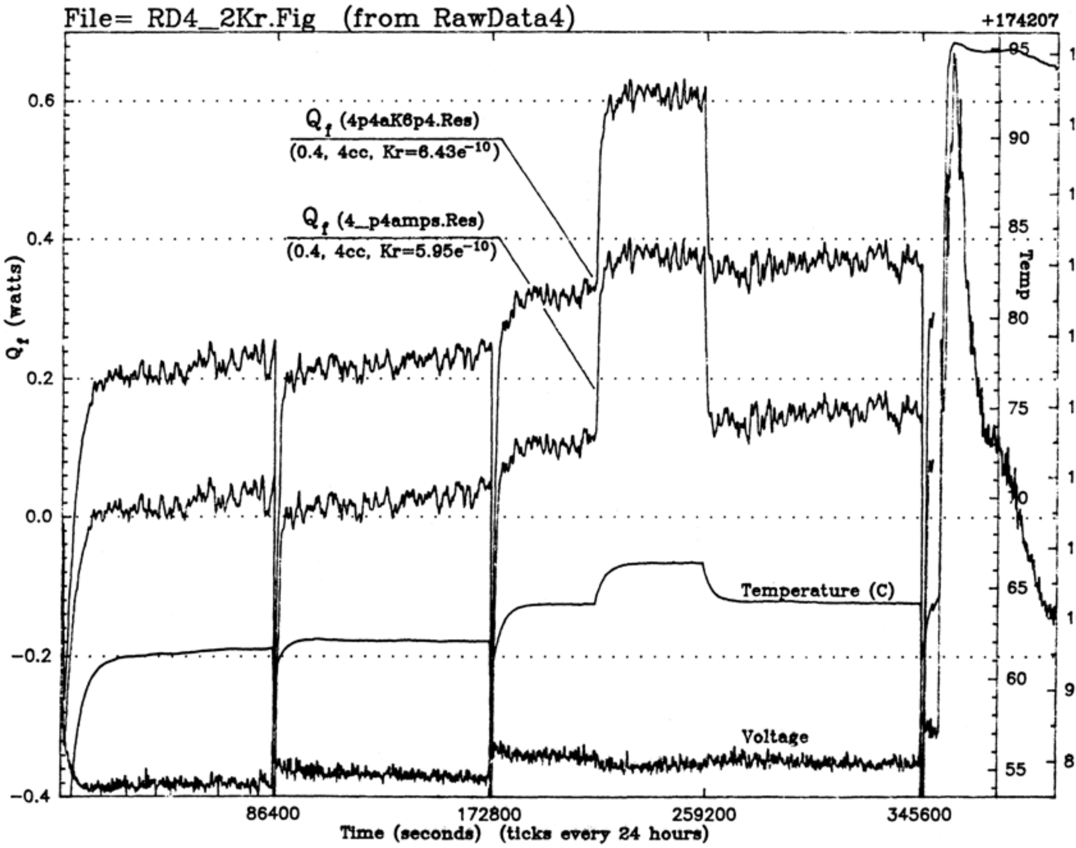

Figure 9. Heatcell 4 run. These results are nearly a duplicate of those from cell 5 except that the data are noisier because of noisier voltage. The upper Kalman filter curve for Q_f is the one demanded by the heat pulse data, 0.270 watts. The lower one is a lower bound, demanded by the fact that Q_f cannot be negative. Note that these data confirm the data of cell 5, including the boil off at the end.

TABLE 3 Fitting Cell 2 Data

Fit	**Range**	**Value**	**% Random Error Estimated**	**Comments**
1.	pts 27-200 from first	K_r=6.52 10^{-10}	2.7	P/F formula
	of 0.4 amps region	Q_r=0.56	19.7	fit M at beginning
	to middle of pulse	M=5.763	2.3	of region
2.	pts 27-350 from first	K_r=6.47 10^{-10}	1.9	P/F formula over heat
	of 0.4 amps reg., past	Q_r=0.536	15.	pulse fit M at beginning
	pulse	M=5.78 moles	2.0	of region
3.	Pts 27-350 over pulse	K_r=6.535 10^{-10}	0.65	Modified Walling formula
		Q_f=0.547	4.8	(MWF)M=5.78, i.c.
				C_{po}=434
4.	Pts 574-836 or to	K_r=6.512 10^{-10}	2.8	Qf=Q_{fo}(l+L)t
	T=93ºC	Q_{fo}=537	22.	M=5.78, i.c.
	No Pulse	L=7.37 10^{-6}	6.7	C_{po}=434
				MWF
5.	Pts 574-792 up to 90º	K_r=6.446 10^{-10}	2.8	Qf=Q_{f0}+ at+bt^2
		Q_{fo}=0.526	23.	C_{po}=434
	No pulse	a=4.467 10^{-7}	151.	MWF
		b=5.319 10^{-11}	12.	
6.	Pts 574-836 or to	K_r=6.758 10^{-10}	3.0	Qf=Q_{f0}+ at+bt^2
	T=93ºC	Q_{f0}=0.712	20.	C_{po}=434
		a=3.85 10^{-6}	17.	MWF
	No pulse	b=1.25 10^{-11}	44.	
7.	Pts 574-859	K_r=6.711 10^{-10}	3.8	Q_f=Q_{f0}+at+bt^2
	entire region	Q_{fo}=0.658	26.	C_{po}=434
		a=5.918 10^{-6}	12.	MWF
	No pulse	b=-2.15 10^{-11}	27.	

Using the data of day 3 it is very interesting that regression analysis can be used to obtain K_r and Q_f without a heat pulse. This has been done in a number of ways. First of all, using points 27-350 of the pulse containing period and allowing the “moles equivalent”, M, of the cell to be fit, we obtain a value of 5.78 moles. This is close to the value we obtain for these cells time and again. Now using this M we fit the data of the next period after D_2O addition. Here we fit for both Q_f and a K_r that is allowed to very with the first and second powers of time, i.e., $K_r = K_{ro} + a\ t + b\ t$, where t is the time after the beginning of this period. As shown in table 3, the agreement with K_r determined by the heat pulse is very good. In fact the values determined by taking data only to 90 deg C are in agreement with those taken to 93 deg, and even those taken to the end of this period, which is close to boiling. All this tends to verify the validity of fitting at these high temperatures in the present case. This cell may be especially well behaved. Notice that the voltage is smooth throughout this period. Most of all, the finding of a solution for K_r in this region which is the same as that given by the heat pulse is strong evidence for internal consistency and the validity of the heat pulse value given. With the heat pulse value correct as given, there must be excess heat as given. Note that the use of data at the highest temperatures isn’t necessary to show the excess heat, but it certainly strengthens the evidence and helps rule out error in the heat pulse data. The same thing can be said of the data below 90 deg in the third 24 hr period.

Taking $Kr = 6.5\ 10^{-10}$ and using data of day 3 up to 90°C, and at this value of Q_f to the end of the day, we can say the following about the results: Q_f (max) is about 1.2 watts or about 20% of the radiative output at 90°C. Near the beginning of the 0.4 amps run Q_f is 0.54 watts or about 14% of the radiative output. The integrated excess heat is about 170 megajoules per mole of palladium or about 1700 eV per Pd atom. This is about 400 times the vaporization energy of Pd for the electrode of cell 2!

Now suppose for some reason we don’t want to accept the given heat pulse value for cell 2, i.e., the 0.27 watts value. What can we say about the results without this datum? For one thing we can expect the excess heat to remain above zero. Suppose we again take an approach that gives us a lower bound on Q_f throughout the run by letting Q_f be zero in the 0.2 amps region at the begining. A Kalman filter calculation is made throughout the run, and K_r is adjusted to set $Q_f = 0$ in the 0.2 amps region. This requires a K_r of $5.95\ 1010^{-10}$. Throughout the 0.4 amps range Q_f still averages about 0.25 watts for three days. The shape of things just isn’t that of a blankcell. In table 4 are shown the values of K_r required at various points to make Q_f equal to zero. Not only is a great range required, atypical of a blankcell, but the shape of Q_f with fixed K_r is unreasonable for a blankcell. Therefore cell 2 appears to be producing large amounts of excess heat, with the amount increasing with temperature.

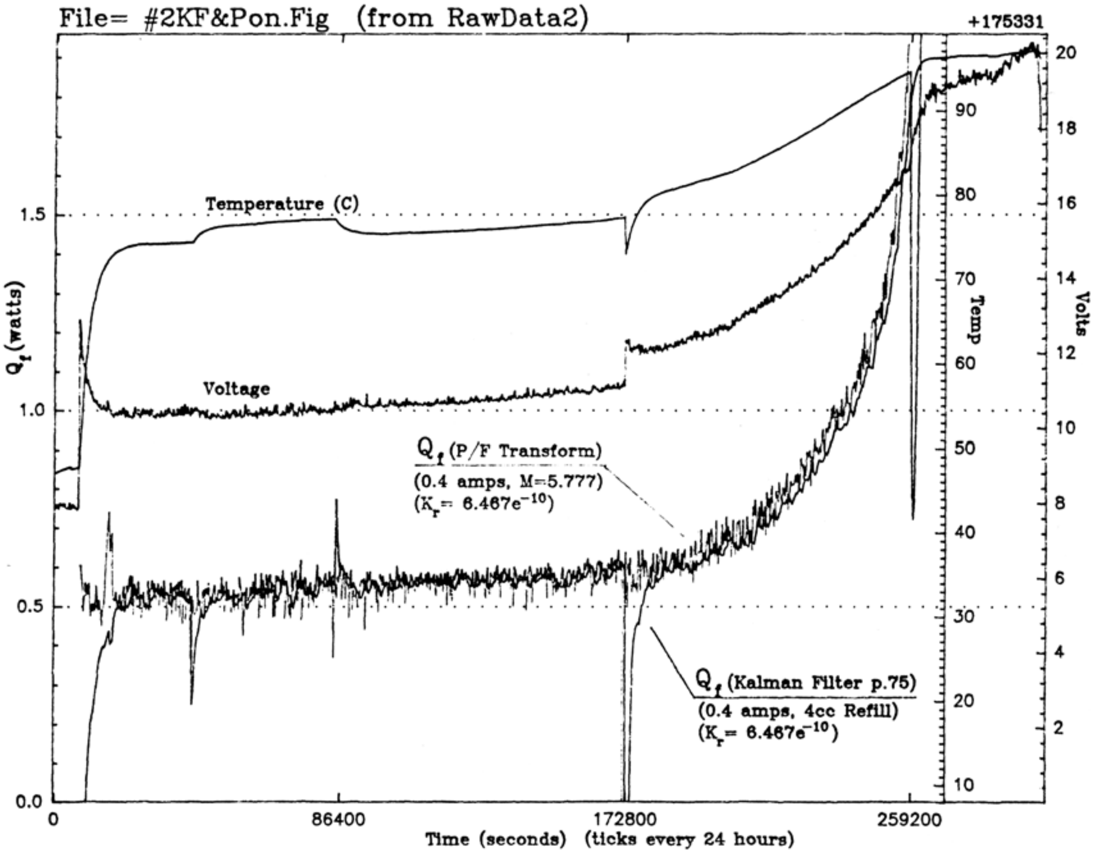

Figure 10. Raw data and calculated Q_f for heatcell 2. Superimposed on the Kalman filter output for Q_f is the Q_f calculated by the full P/F equation for the model. Note how the Kalman calculation is a real-time low pass filter, and cannot follow rapid changes in temperature.

TABLE 4
K_r Values Required for Q_r to Be Zero
Cell 2

Point	Time	Temp	K_r (to force $Q_f = 0$)
576	173387	74.763ºC	$5.69\ 10^{-10}$
600	180587	79.760	$5.618\ 10^{-10}$
650	195587	81.689	$5.609\ 10^{-10}$
700	210587	83.844	$5.579\ 10^{-10}$
750	225587	87.014	$5.497\ 10^{-10}$
792	238187	90.026	$5.322\ 10^{-10}$
(792, 793, 794)	average		$5.322\ 10^{-10}$
(790, 791, 792)	average		$5,352\ 10^{-10}$
800	240587	90.578	$5,352\ 10^{-10}$
859	258287	94.434	$4.498\ 10^{-10}$
(2-23) P/F formula		47.109 to 47.704	$5.725\ 10^{-10}$
(2-23) MW formula		47.109 to 47.704	$5.746\ 10^{-10}$

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ANALYSIS OF PONS/FLEISCHMANN CALORIMETRIC DATA

Part Two

In part two we continue to discuss members of the set of silvered cells which we have analyzed. Most of the space will be allotted to the cell 6 experiment because of its great significance in the whole study. We will also include a short discussion of cell 7. Both are heatcells with 0.1 F LiOD in D_2O as electrolyte and Pd electrodes.

ANALYSIS OF HEATCELL 7

There is no blank for this run, and there are no heat pulses applied during the run. Also we have found no good places during the run to solve for K_r, Q_f, and C_p all together. Figure 1 shows what we get for Q_f using a Kalman filter with K_r taken as a conservative $5.95\ 10^{-10}$ (That is the K_r for cell 3, a blankcell, the lowest we have found in this set of cells.) A modest excess heat is indicated, but we have found no compelling proof of it.

ANALYSIS OF HEATCELL 6

In figure 2 are shown the raw data for cell 6. Notice the two current ranges. In the 0.2 amps period the temperature is low and unusually steady. The voltage is noisy (probably because of bubbling) but very useable. In the 0.4 amps range the temperature rises smoothly to boiling. A unique feature of this run is the presence of four heat pulses. Once again the power of the pulses is 0.27 watts (actually 0.272 watts in the present case). There is even a pulse of the same wattage in the high temperature region. This gives us a chance to compare output pulse heights in the two temperature regions, examine internal consistency, and further test the validity of the model.

In figure 3 is shown the Kalman filter output of Q_f as a function of time. Here a value of $8.0\ 10^{-10}$ is used for K_r. It is clearly the value demanded by the heat pulses. This can be seen by inversion of data through the region of any heat pulse or by insisting that the Kalman filter output be a square pulse of height 0.272 watts. While this large heat coefficient is easily understood as caused by a little gas spoiling the vacuum of the cell dewar vessel, the fact that it happens in the largest heat producing cell is puzzling. We will speak more of this later. It should be understood here that there is no mistake concerning what Pons gives as the heat pulse wattage. In yet third discussion of this subject, on May 21, 1991 Pons told me personally, and another who had helped run the experiments verified, that they had always used 0.27 watts in the heat pulses of this set, a constant current of 50 milliamps through a precision, temperature insensitive resistor string. This gave a measured voltage drop of 5.44 volts in the case of cell 6, or 0.272 watts.

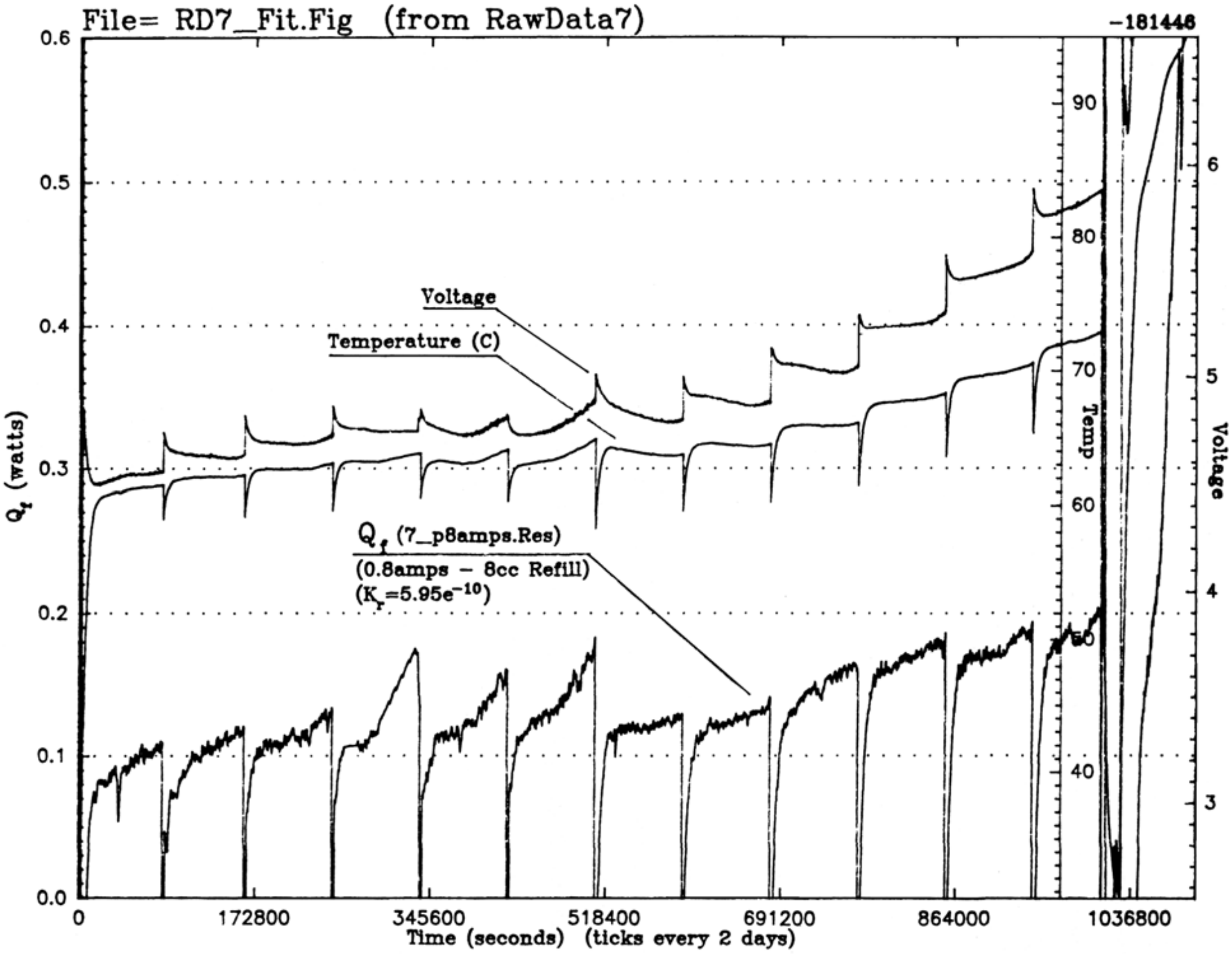

Figure 1 of Part Two. Raw data and Kalman filter calculation of Q_f for Cell 7.

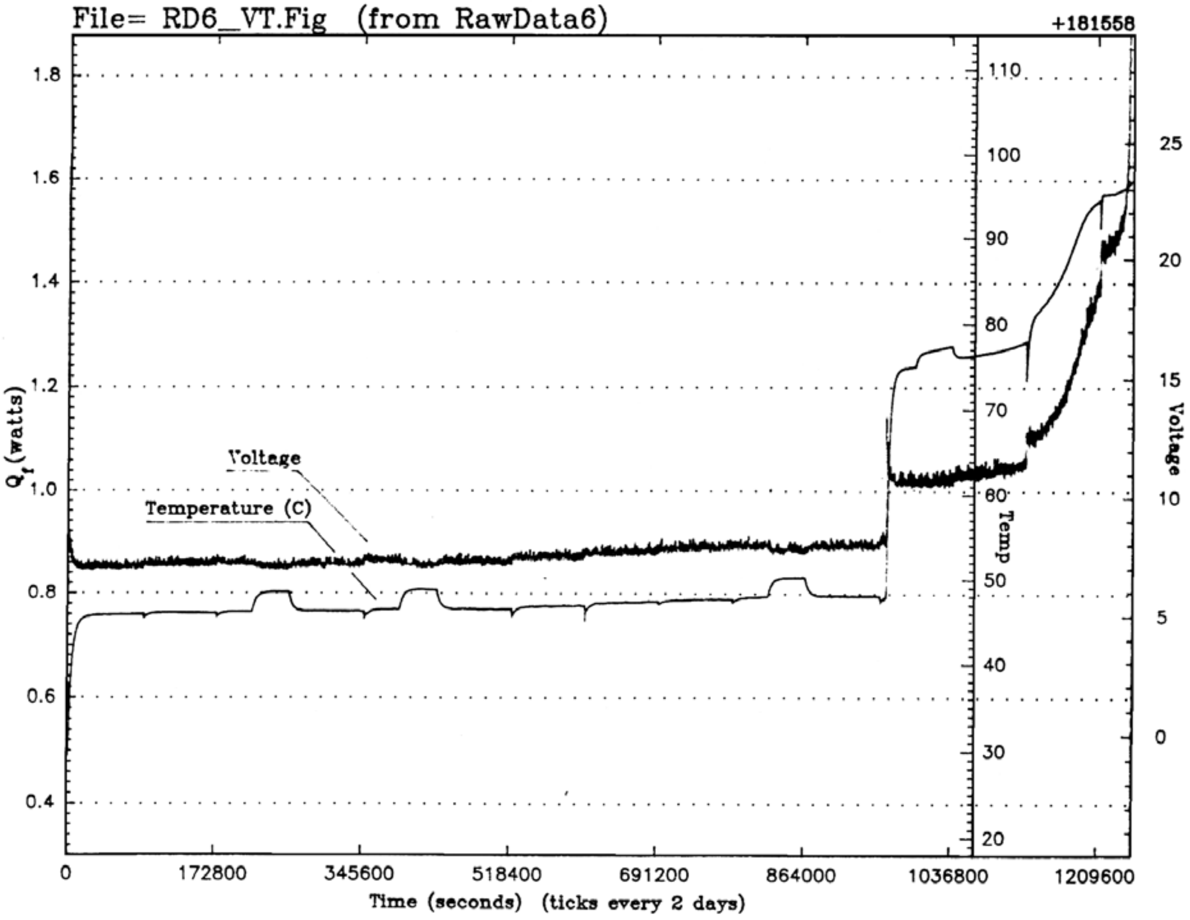

Figure 2 of Part Two. Raw data of Cell 6 experiment. Current is 0.2 amps for 11 days, then switched to 0.4 amps

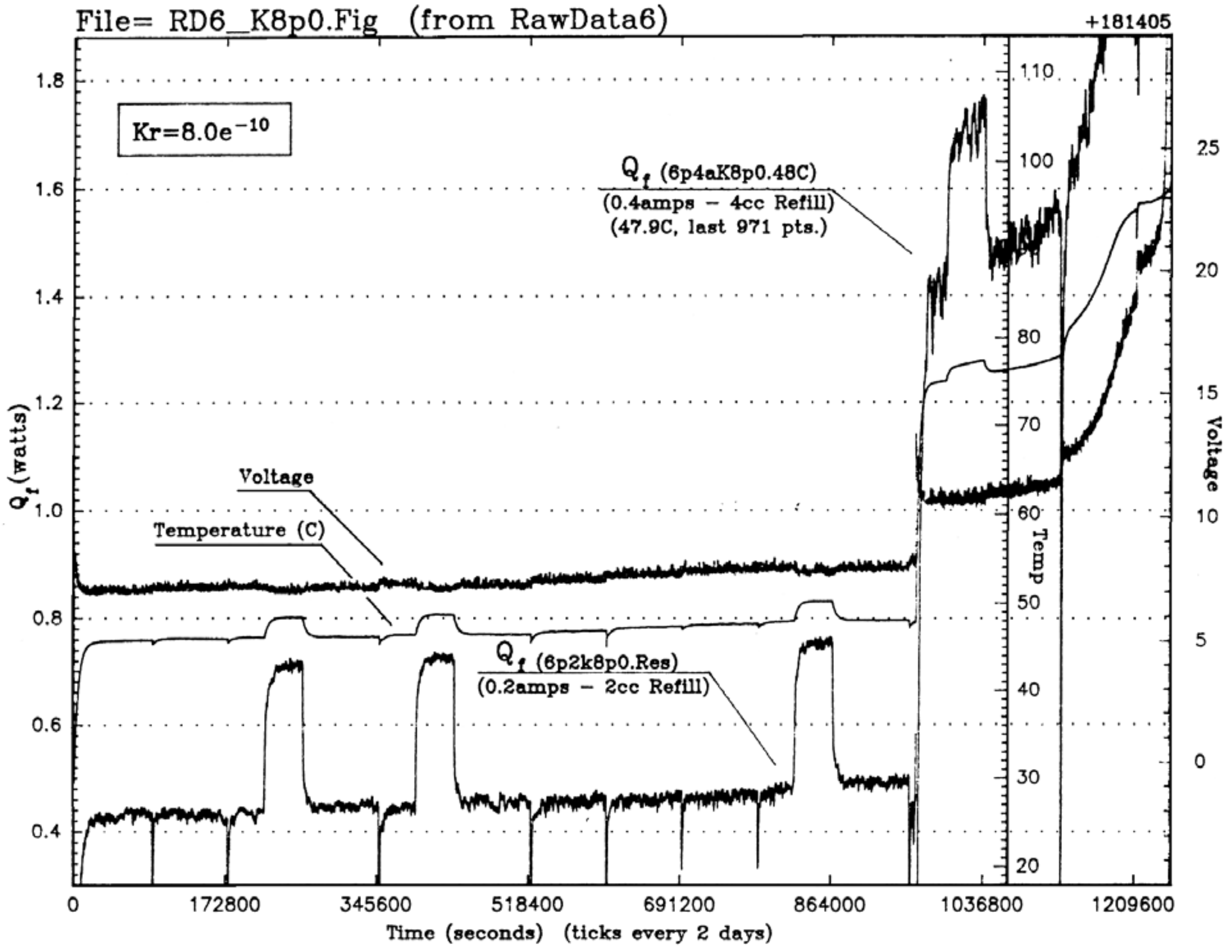

Figure 3 of Part Two. The Kalman filter output of Cell 6 using a K_r necessary to make the pulse height equal to 0.27 watts

In figure 4 is shown the total excess heat input, Q_f + HP, calculated in three different ways, by Kalman filter, by P/F model formula, and by MWF. They all agree well except in the highest temperature region, i.e. in the region beyond the last heat pulse. Here the MWF calculation deviates. This is to be expected because the P/F formulation was used in the Kalman filter and the MWF approach doesn't account for vapor evolution in such a detailed way. It should be noted that even though the non-filtered calculations look very noisy, especially in the high temperature region, all of the information is there, and a statistical analysis of the data yields well defined values of Q_f and of the heat pulses, HP.

It would be a nice confirmation of the large K_r dictated by the heat pulses if an analysis of data in a no heat pulse period gave a similar result. The most likely place to look is day 13 outside the heat pulse period and day 14. We have done this, and do indeed get by regression analysis a value of K_r similar to that obtained by using the heat pulses. We have gotten similar results using the P/F formulas and the MWF approach. By allowing Q_f to vary quadratically in time, and solving for K_r and Qf using points from T < 90 deg C, we get K_r 7.74 10^{-10} and Q_f at 1.126 mega seconds of 1.46 watts, going up quadratically from there. We also get a solution using the MWF formula. Here $K_r = 7.810^{-10}$ and $Q_f = 1.49$ watts. Other periods might also be present in the data which give solutions. We have not exhausted the possibilities.

If this analysis holds, and we see no way around it at the present time, the excess power of cell 6 is impressive indeed. The excess power is about 1.5 watts for the first two days of the 0.4 amps region. The electrode is small, 1mm dia by 1.25 cm long. Counting the 0.4 amps period and the 0.2 amps period, there is about 6000 eV per Pd atom excess energy, or over a thousand times the energy required to vaporize the electrode. Putting it this way it is easy to see that we are not dealing with known chemistry or metallurgy. At issue is a profound energy source. It is of utmost importance that these results be reproduced.

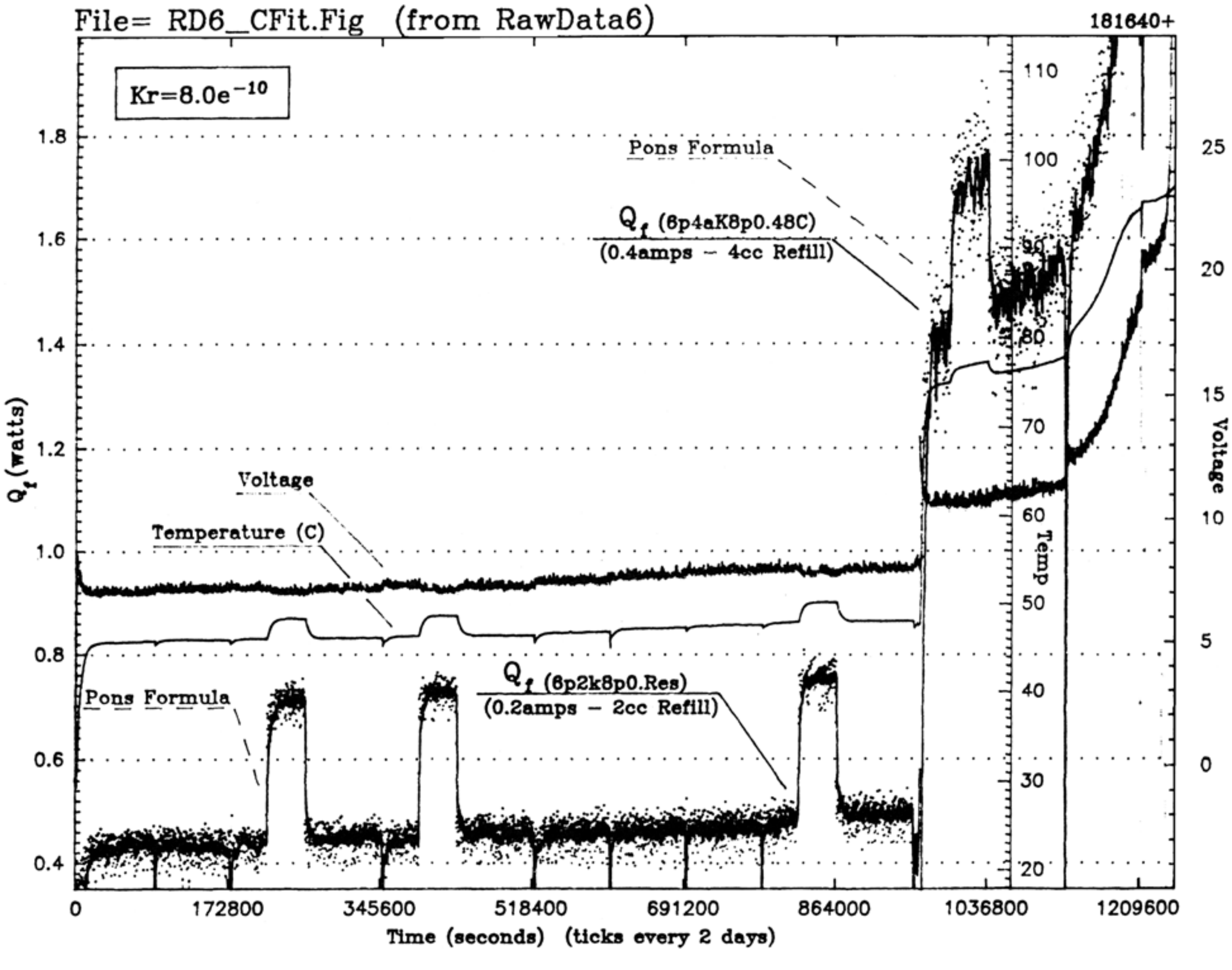

Figure 4 of Part Two. Raw data and calculated data for Cell 6.

SPECIAL POINTS

In this section we will discuss a number of special points that have come up during the analysis. This analysis has been far from exhaustive even though we have spent some months on it. We have gone further than reported here in a number of ways, but some things have not yet been formalized in report form. For example, we have redone much of the regression analysis using both a radiative heat transfer coefficient, K_r, and a conductive coefficient, K_c, in parallel. We now believe this is the correct way to do it. However, the use of K_c tends to increase Q_f, so the use of K_r alone was a conservative approach.

The use of heat pulses as a calibration of cells easily can be shown to be completely valid as far as the mathematics is concerned. Let us discuss the physics. The heaters are placed inside the cell in a position approximating that of an electrode. The response of the cell to heat from the resistors would be the same as the response to Q_f generated in the electrode. The heat pulse can be applied any time. When the analysis is carried out "exactly" as we have done, the pulse can be of any time duration, so long as good numerical derivatives are possible. In the data we have addressed the pulse was maintained at a constant power long enough to reach a new steady state, presumably to facilitate analysis. We encourage the frequent use of heat pulses in the future in this type of work. For example, if blankcells had frequent and carefully placed heat pulses, not only could the K_r be determined, but the K_r, K_c and C_p of the cell could be determined, and at various temperatures. Also the degree to which the cell analysis is valid could be checked in detail. For example, if the heat pulses get reproduced correctly by the analysis at 93 deg C then the analysis is valid at this temperature. After all, the end purpose of the analysis is to determine unknown heat production, Q_f.

On the matter of heat transfer out of the cell, we believe that it should be represented by $K_r(T^4-T_b^4) + K_c(T-T_b)$, where K_r and K_c are the radiative and conductive heat transfer constants, and T and T_b are Kelvin temperatures of cell and bath. These act in parallel. The K_r can be expected to remain constant because it depends mainly on geometry. It can be approximated by blackbody theory, but glass surfaces are not blackbodies because of the 5% or so specular reflection and because they are semi-transparent in the near infrared. Water and heavy water are also semi-transparent in the near infrared, but D_2O has a different spectrum than H_2O in the near infrared and in the mid infrared. The main radiation flux involved is in these spectral regions, and the wavelength in the infrared at which the electrolyte becomes opaque is shifted a great deal by the mass of the deuteron being twice that of the proton. Therefore, the emissivity of a cell probably varies with the electrolyte. In any case, the K_r is surely less than that calculated by blackbody theory. It should be constant, however, from run to run and even from cell to cell. The conductive part, however, easily changes by a little outgassing into the vacuum jacket. K_c can be expected to vary from cell to cell and perhaps even with temperature and time. One technique, then, is to fix K_r at some reasonable value, say, $5.0\ 10^{-10}$ or $5.5\ 10^{-10}$ and fit K_c by the data instead of fitting K_r. One advantage of this procedure is that detailed fit math now works with T instead of T^4, and less precision is required. Also the model is closer to reality.

When looking at the overall results of this study it will be noticed that there is a correlation between excess heat and the size of K_r. One would expect none. Some have suggested that this correlation is unacceptable and that the data must be wrong. Of course anybody's data "could" be wrong. It is also often the case that correlations show up when they aren't expected. In the present case we can think of at least one possible reason for a correlation. It has recently been reported by researchers that He is produced by cells generating excess heat. It turns out that He readily diffuses through pyrex glass. Perhaps excess heat is accompanied by He which spoils the vacuum a bit increasing K_c enough to give the high heat transfers found. A quick calculation indicates that there might be enough He to do it. Of course there also might be simpler explanations.

In this study we use the mathematical models of Pons and Fleischmann and C. Walling. The P/F models are discussed in references [1-5]. The Walling formula was in an unpublished work given to me by Walling. We modified it to use $(T^4-T_b^4)$ instead of (T^4-T_b), and further to use both K_r and K_c.

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