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Analysis of Some Electrochemical Calorimetry Data

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To demonstrate our techniques for analyzing the calorimetric data of an electrochemical cell, we use three sets of data taken at the NEH laboratory in Sapporo, Japan, copies of which were kindly given to us by Dr. Melvin Miles who was personally involved in their taking. The code names for the data sets are M7c1, M7c2, and M7c3. All were run in similar F/P silvered electrochemical cells (see Figure 1) with the same daily programs for cell current, bath temperature, calibration heat pulses, etc. All were run looking for "Cold Fusion" type excess energy production. Each cathode is a palladium alloy of interest in the field. Data of temperatures, voltage, current, imposed heat pulse value, and bath temperature were taken every 5 minutes. The detailed equations of the analysis are discussed elsewhere [1].

The objective is to fit the data with the physical model that is based on best fit values of the effective mass of the cell contents, M, the conductive heat transfer coefficient, Kc, and the excess heat, q. The model relies on being able to calculate all powers (energy flows) at all times. Especially important is the appearance of excess power (excess heat, q) which may be of nuclear origin.

Key to the analysis is the use of physical facts as well as mathematical techniques. For example, the heat transfer coefficients should not be affected directly by the presence of excess power. Multiple linear regression analysis will be used extensively. The goodness of the results and proof of excess heat (or the lack of it) is the ability of the resulting calculated parameters to correspond with reality. Experience and judgment are essential to this process.

Note that we use both Kr and Kc in parallel as components of a total heat transfer coefficient, K, in a sense. But since Kr and Kc have different dimensions, their magnitudes have very different meanings, and they cannot be compared directly. Between two temperatures T1 and T2, one energy flow is proportional to Kc(T2-T1) and the other to Kr(T2^4-T1^4). The total energy flow is the sum of the two. Past experience with calculations and measurements of the heat transfer properties of silvered F/P-type cells has shown that while Kc generally accounts for only about 10% of the heat transfer process, it is Kc that changes, due mainly to changes in liquid level or in the current with its resultant stirring changes. Kr is reasonably held constant (due to the silvering of the cells) at a value previously determined, while Kc is allowed to vary as needed to keep the total heat flow proper. The overall fit is not very sensitive to what fraction of the heat flow is blamed on Kc. For the small heat pulses used (0.250 watt), Kr and Kc are constant as the temperature, T, changes so long as current doesn't change. Computer calculation time is hardly an issue, requiring only seconds at most.

Data Set M7c1

Figure 2 is a record of the temperature of the cell M7c1 over the first one third of the run. The hump-like changes in T are due to the 0.250 W heat pulses, while the step-like changes (large and small) are due to current changes.

To begin our analysis we select a time range within the first constant current region over which to determine an average q, M, and Kc. Giving time for initial electrode charging, we start at, say, 2000 min. and stop after the last heat pulse at about 14000 min. Entering the times, the regression calculation provides the following output of the best fit values for average q, Kc, and M, including the standard deviation "sigma" of each and the degree of dependence "dep". The rows of numbers below correspond in position to the rows of labels.

```
range start  range end  sigma of data          dep of q
q                   Kc                     M       dep of Kc
sigma of q sigma of Kc        sigma of M       dep of M
```

```
asig =
2.0000e+003  1.4000e+004  1.3387e-002  9.7039e-001
8.5714e-004  3.0332e-002  5.6124e+000  9.7039e-001
1.5876e-003  2.8960e-004  2.6851e-002  2.6326e-001
```

The fit is beautiful, as seen by the small sigmas, the reasonable value of M, and the small value of q. Note that the dependency of M is small compared to that of q and Kc. But that of Kc and of q are far enough away from unity to allow good determination of both. The main result seems to be definite; there is clearly no excess heat in this region. Various schemes can now be used to analyze the rest of the run.

Let us first calculate Kc over the entire data range of Fig. 2 by holding q, and M constant at the values determined initially above. We will compare changes in Kc with what we know to be physically reasonable to increase our confidence in the value of q. For example, we expect large excursions in calculated Kc (called "outlyers") with sudden changes in power as at the beginning and end of heat pulses, when water is added to the cell or when the current changes, due to the time constant of its determination. We also know that Kc must stay constant through the outlyers of the heat pulses, but may shift in value due to changes in liquid content and current. Gradual changes in Kc due to evaporation and the lowering of the water level are seen as a gradual slope in Kc (called the "tidal effect"), while additions of water are seen as discontinuities in Kc with outlyers. Confidence in a particular value of q depends on whether the calculated Kc using that q behaves as expected. A value of zero for q is always a reasonable initial guess, even if the initially determined average q isn't. Figure 3 shows Kc at every point assuming q=0 and M equal to the 5.61 moles D2O equivalent. Careful examination of the Kc points shows that they are continuous (except for outliers) across the heat pulse corners and otherwise correct for a fit, and exhibiting the expected tidal effect. In Fig 4 we show Kc calculated for the entire M7c1 run. In Fig 5 we expand a section of Fig 4 to carefully examine the continuity of Kc. There are no water additions or current changes in this region. The requirement that Kc be continuous through a heat pulse is a powerful test-of-fit, and shows conclusively that to the accuracy of the data, the excess heat is zero. When these guesses of q and M are applied to the rest of Run M7c1 we obtain similar results. Excess heat = 0.

If we wish to look at the data more closely there are a number of things we can/must do. All data have a level of accuracy that varies from place to place within a set. Sometimes this level is knowable, while sometimes it is not. In the present case, for example, the current is programmed ahead and intended to be rigorously controlled by the apparatus. Fortunately it is also measured and recorded in these data sets. Fig 4 shows the actual current throughout M7c1. Note that it is not as planned in some places! These points should be avoided, including regions near the end of the run. Unfortunately other vital data was not recorded. For example, in the present data sets, there is no record of a measurement of the heat pulse power. We must rely on the analysis to discover if the heat pulses are as planned. We can not tell exactly when the pulses went on and when off, and we don't know exactly their value.

All data also have a level of precision that can be difficult to know. Our techniques make most of this easy to view. To see how the random noise in q varies throughout M7c1 consider Fig 6. Outside the dark regions the points are mostly outliers, and are justly left out of calculations. These points are useful, however in showing where the heat pulses start and end, and in showing the disruption by water additions. The width of the dark region is surprisingly varied. It is a direct result of the experimental errors, shows directly the random error that is imbedded within the data set, and is a limitation on accuracy obtainable from the data. Note, as an example, that a large error is unavoidable toward the end where the current control is fowled up.

Data Set M7c3

The NEH data set M7c3 has also been analyzed as explained above. It too shows an excess heat of zero. The precision in the data as seen by the noise in q varies considerably from the M7c1 case, as shown in Fig 7.

Data Set M7c2

We now consider the M7c2 run which may involve the production of excess heat. The cell temperature, see Fig 8, looks much like Fig 2. However, analysis of the same initial range (2000 – 14000 min.) as for M7c1 (low constant current) shows a different behavior. Dr. Fleischmann has analyzed the first heat pulse region [2], and we will analyze that same region by our means for comparison.

Taking the first heat pulse range (3000 – 4200 min.) and solving for the average q, Kc, and M we get

```
range start  range end  sigma of data  dep of q
         q           Kc         M             dep of Kc
sigma of q sigma of Kc  sigma of M     dep of M


asig =

  3.0000e+003  4.2000e+003  1.1932e-002  9.7011e-001
 -4.6549e-002  2.1070e-002  5.5584e+000  9.7011e-001
  4.4549e-003  7.3440e-004  6.4418e-002  2.6334e-001
```

Notice that we get a negative q and an unreasonable value for Kc (only two-thirds the value from M7c1)! Both signal that something is unusual. In our calculations and fit we assumed that the heat of the heat pulse did not trigger any change in other sources of heat, such as nuclear additions to q. If such a source increased its input as the temperature increased, that would be like putting in an incorrect heat pulse. It would also be unknown in magnitude and shape—invalidating our multiple regression analysis. This could explain the peculiar results. A way to show this directly is to consider the M7c1 case for the same heat pulse. If we use in our calculations a value for the heat pulse power that is 10% or so lower than it really is, the q in that region will incorrectly come out negative, and the Kc will calculate to an erroneous low value. This is just what Fleischmann calls "positive feedback", with excess power of Cold Fusion increasing proportionally with the increase in temperature due to heat pulses, etc., manifested by the negative q and small Kc described above.

Our technique allows us to easily calculate the real q at each data point in spite of the initial problems with q and Kc by using appropriate values of M and Kc. We use the value for M initially determined above, since M doesn't change much, especially in this low T region. We use the value for Kc from our analyses of the M7c1 cell that is similar and shows a q of zero with no feedback at all. Or the M and Kc of the cell "blank" could have been obtained by running a short run with, say, a cathode that was known to give q=0 everywhere. The calculated q, shown in Fig 9, is similar to that obtained by Dr. Fleischmann for this same data by a different route [2]. Similar results are seen in the other pulses throughout the low current range of M7c2.

The big question is, of course, "How evident is it that cold fusion type excess heat has been observed in the M7c2 run?" After all that's what the experiments are all about. The answer is far from simple! Excess heat is a possible solution of the anomalous data. But we can't be certain of excess heat until all other significantly possible causes have been considered and eliminated. Certain possibilities like a systematic error in the temperature that could give a negative q are eliminated because they do not fit other aspects of the anomaly. But others do fit the anomalies. For example, we have no direct data to prove that the heat pulse was 0.250 watt as it was supposed to be because no actual measurements of the heat pulses were recorded. It is not likely, but perhaps the pulse controller was fowled up analogous to the current controller in the M7c1 run. Perhaps careful working of the data will show some other problem. Another possibility might be fragments of palladium floating in the electrolyte and catalyzing recombination proportional to the temperature. Still others might involve adjustments with the cell that aren't recorded. We can say that the 35 milli-watts or so for max q is outside any expected random error. Yet systematic error can come in any size and is always a possibility, and so must be treated differently than random noise. The researcher must carefully reduce the probability of significant systematic error to a negligible level. In the present case we are reduced to recommending that the experiment be repeated. That is easy to say but hard to do!

Let us try to extract more information regarding the possibility of excess heat or other problems with the experiment from the data. In favor of real excess heat is the calculated q of Fig. 9 that more or less follows the temperature change of the heat pulse, giving it a distinctive shape. This shape and size repeats itself throughout the initial current region at the pulses. Similar effects show up in other regions. Another indication is the q > 0 needed to make Kc continuous through a heat pulse in a constant currant region. Calculated Kc in Figure 8 used q = 0 as the guess. The smaller narrower decreases in Kc throughout the low current region (before the current increase at 14000 min.) correlating with increased temperature of the heat pulses indicate that q = 0 is too small. Increasing q allows Kc to be continuous through a few of the heat pulses.

On the other hand, the increase in calculated q of Fig. 9 is just what happens to q with any q = 0 cell data set when a Kc value too large is used. The "excess heat" calculated with Kc too large looks just like that of data M7c2 in Fig 9, but in this case the heat shows up because the input data (Kc) is flawed. Therefore the detailed shape of Fig 9 suggests that the data of set M7c2 may also be flawed, and the first guess is that the flaw might be in the calibration pulse, making the presence of real anomalous excess heat as shown in Fig 9 doubtful. A second and more likely guess is unreported cell over-filling, discussed below.

Further analysis of the data reveals other behavior that violates the model and points to unreported problems with the experiment and possible explanations of the "excess heat". Somehow the calorimeter is not behaving as modeled and as fitted in the case of M7c1. For instance, consider the calculated Kc in Fig. 8. (Note the the Kc outlyers help orient Kc with the heat pulses, changes in current, and other phenomena.) There are large abrupt increases in Kc within regions of constant current at about 2500 min, at 10000 min, and at 20000 min., the later coming back down as the current is lowered at 22000 min. If true, these changes represent drastic changes in cell behavior and can be accepted only if caused by unreported non-modeled behavior like, perhaps, overfilling. Overfilling means the electrolyte comes in contact with the cell cap, increasing the area of heat conductance and Kc. As water evaporates, the level lowers but surface tension keeps the surface in contact with the cap, until finally it breaks free and Kc is reduced, as demonstrated at about 4200 min. Close examination of Fig. 8 reveals that the heat pulse corresponding to q of Fig. 9 while the cell was over-filled from about 2500 min. to about 4200 min. and Kc was unusually high. It may be that the Kc used to calculate q in Fig. 9 is just too high because of the over-filling problem. Another hypothesis is that the increase in temperature due to the heat pulse causes increased pressure in the over-filled cell and changes Kc, while the model assumes it remains constant, thus producing an artificial excess heat. Either way, it is clear that unreported cell adjustments and problems make it impossible to confirm real Cold fusion excess heat with this data set.

One more way to try to determine the real value of q is illustrated in Figure 10. Assuming a well behaved calorimeter, we can believe that Kc will be fairly constant (except for the tidal effect) as the current is constant, and that q cannot be negative (never act as in a refrigerator). Varying Kc within a realistic range and calculating q over the entire data set, we can determine that the real q curve will be the one most well behaved over the entire range. Thus it may be reasonable to believe that the real value for q lies near the level of the red curve of Fig 10, i.e. near zero, within the statistics of the data.

[1] Wilford N. Hansen, Galen J. Hansen, and David Glenn, "Vacuum Dewar Electrochemical Calorimetry and Analysis Using Statistical Methods", submitted for publication.

[2] M. H. Miles, M. Fleischmann, and M. A. Imam, "Calorimetric Analysis of a Heavy Water Electrolysis Experiment Using a Pd-B Alloy Cathode", Naval Research Lab, Washington, DC 20375-5320, NRL/MR/6320—01-8526.

Figures

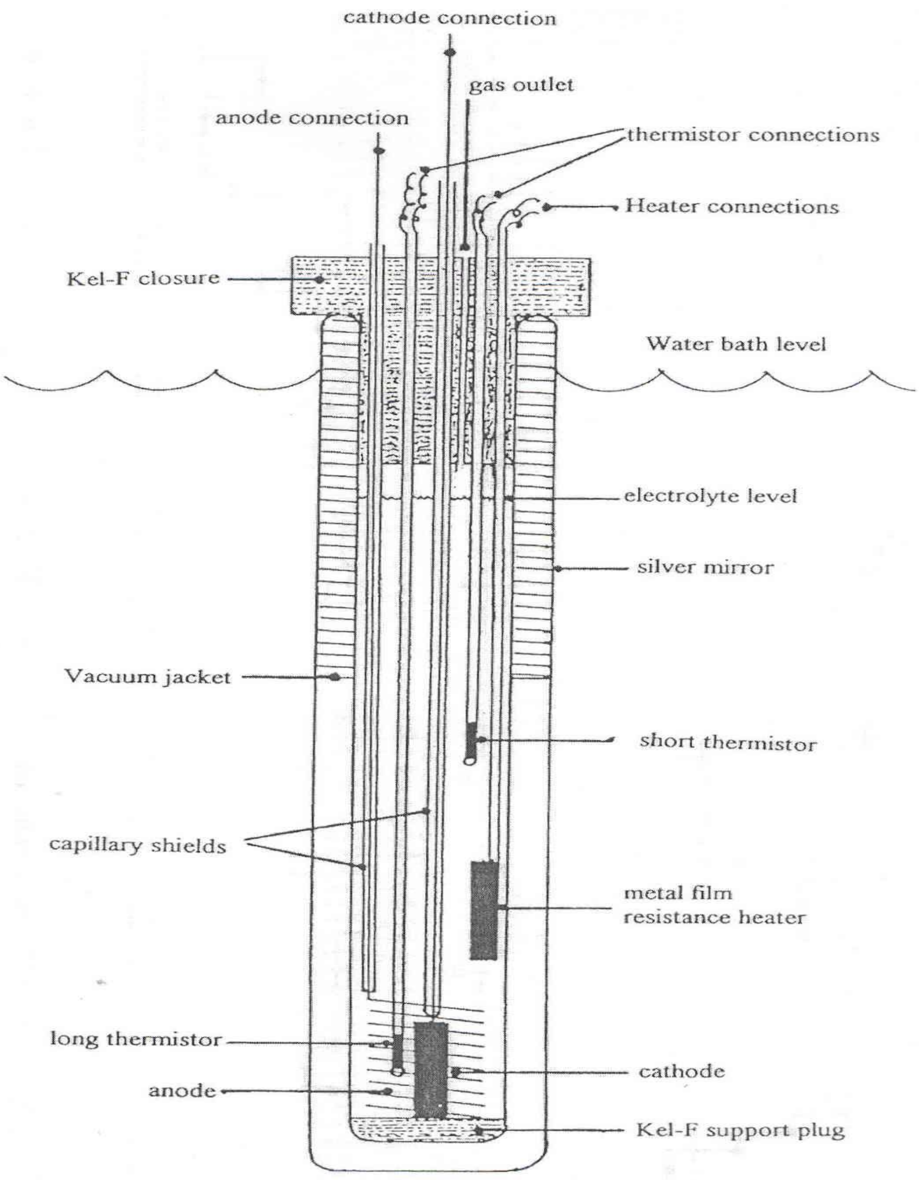

Fig 1. This is a model of the F/P cell used in taking the data analyzed herein.

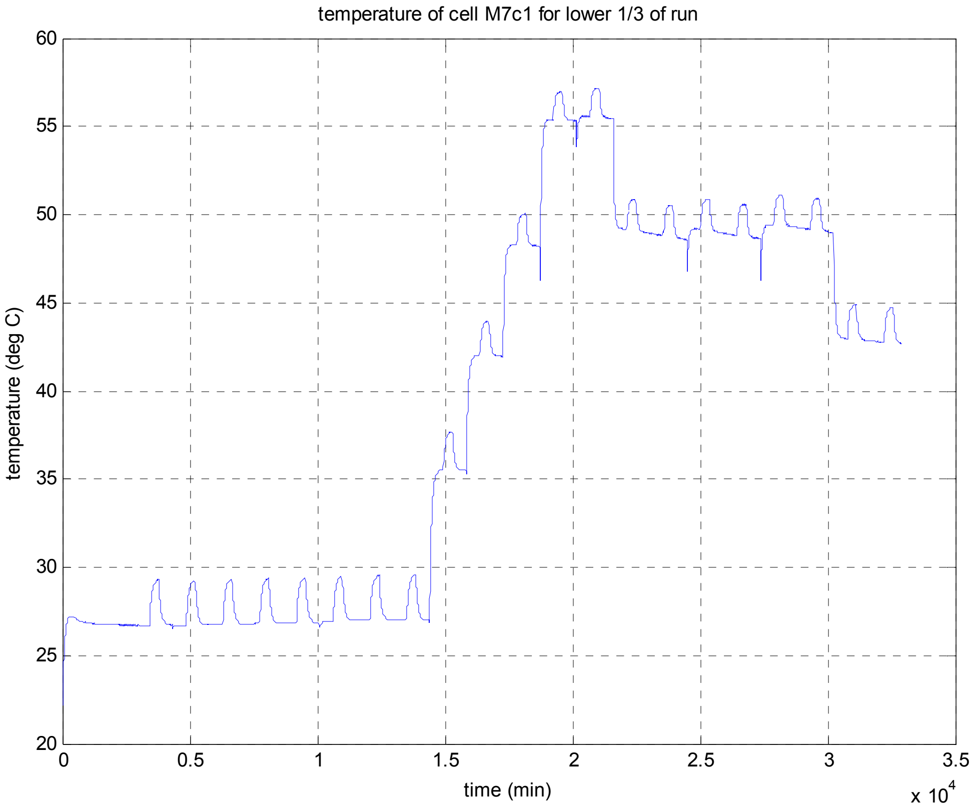

Figure 2. This is the temperature of Cell M7c1_lo. The humps are rises due to regular calibration power pulses of 0.250 watt. The breaks in the temperature level for groups of humps are due to current level changes.

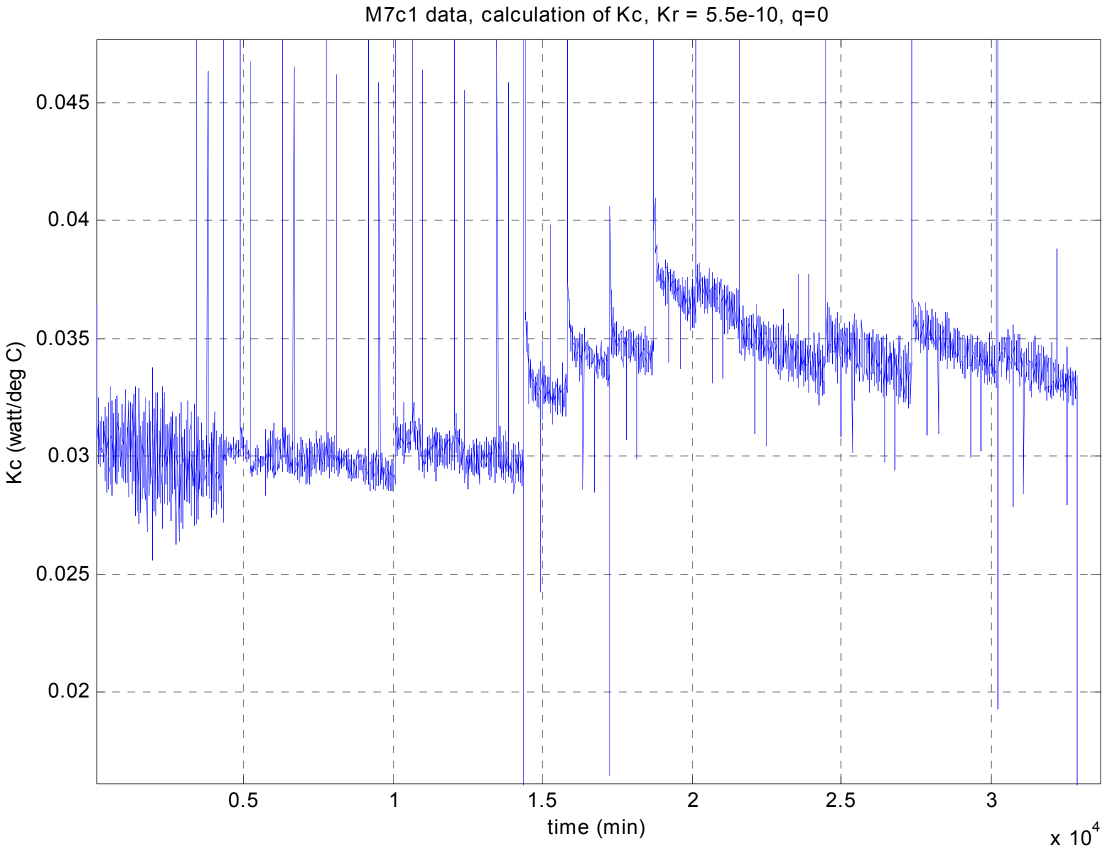

Figure 3. This is the conductive heat transfer coefficient fit for M7c1_lo. Note the slope due to lowering of liquid level between fillings. Kc does not otherwise change across a heating pulse (pulse location shown by outliers), but does change as the current changes as expected because of changed stirring.

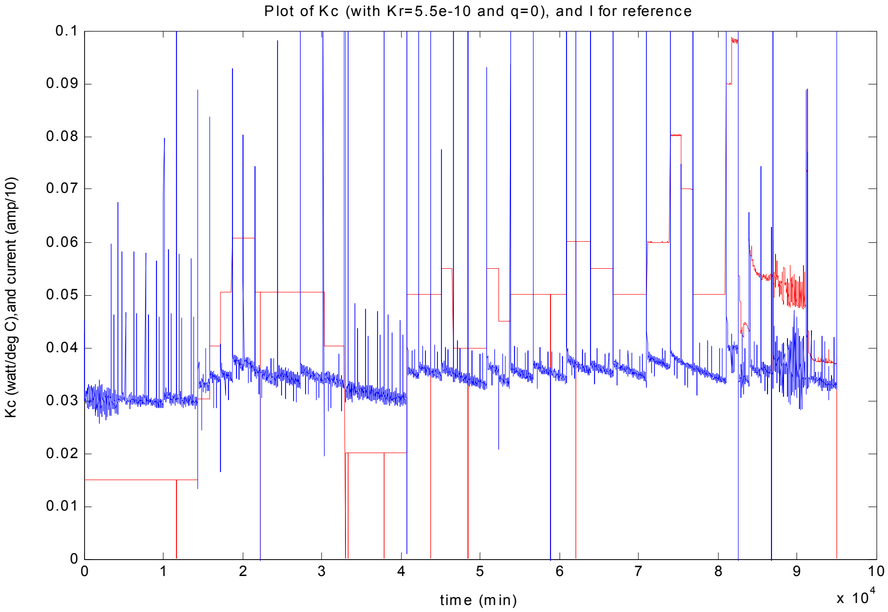

Figure 4. This is the Kc fit for the entire M7c1 run. The current is also shown and is somewhat complicated by controller malfunction, especially at the right end. Q is near zero everywhere.

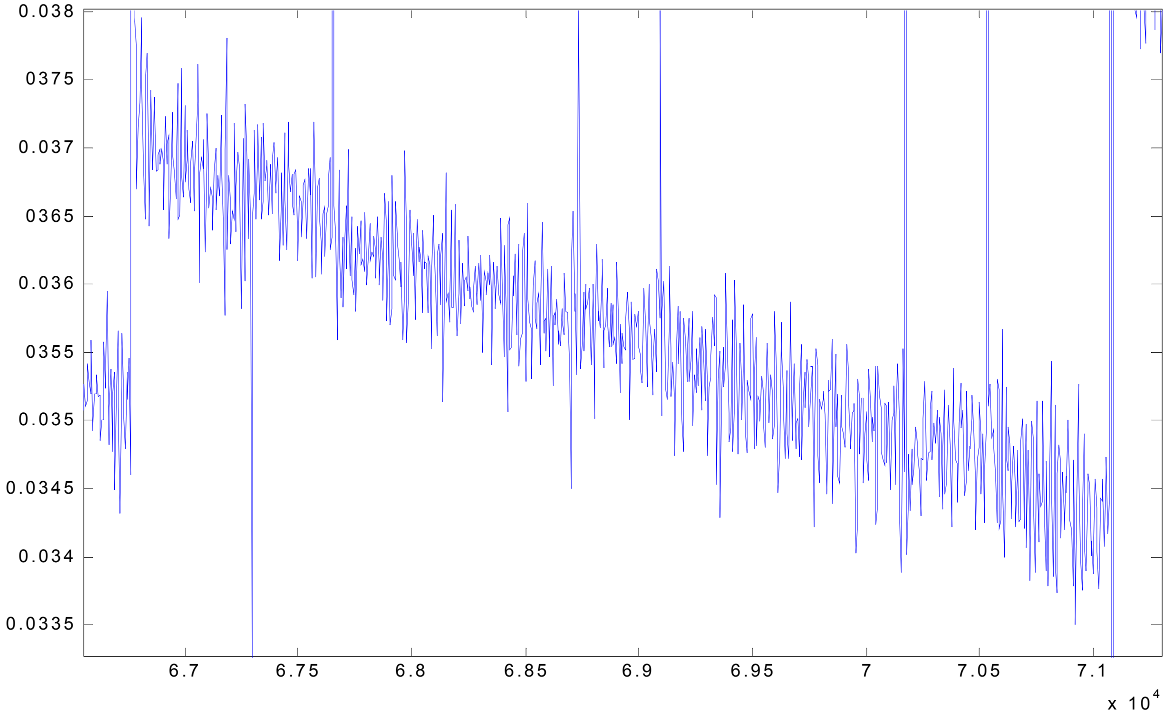

Figure 5. This shows a part of Fig 4 expanded. Note that Kc is continuous through the heat pulses, a criterion for good fit. Multiple linear regression across a heat pulse and including points on either side is the best criterion, provided the excess heat, q, does not change appreciably throughout the pulse region.

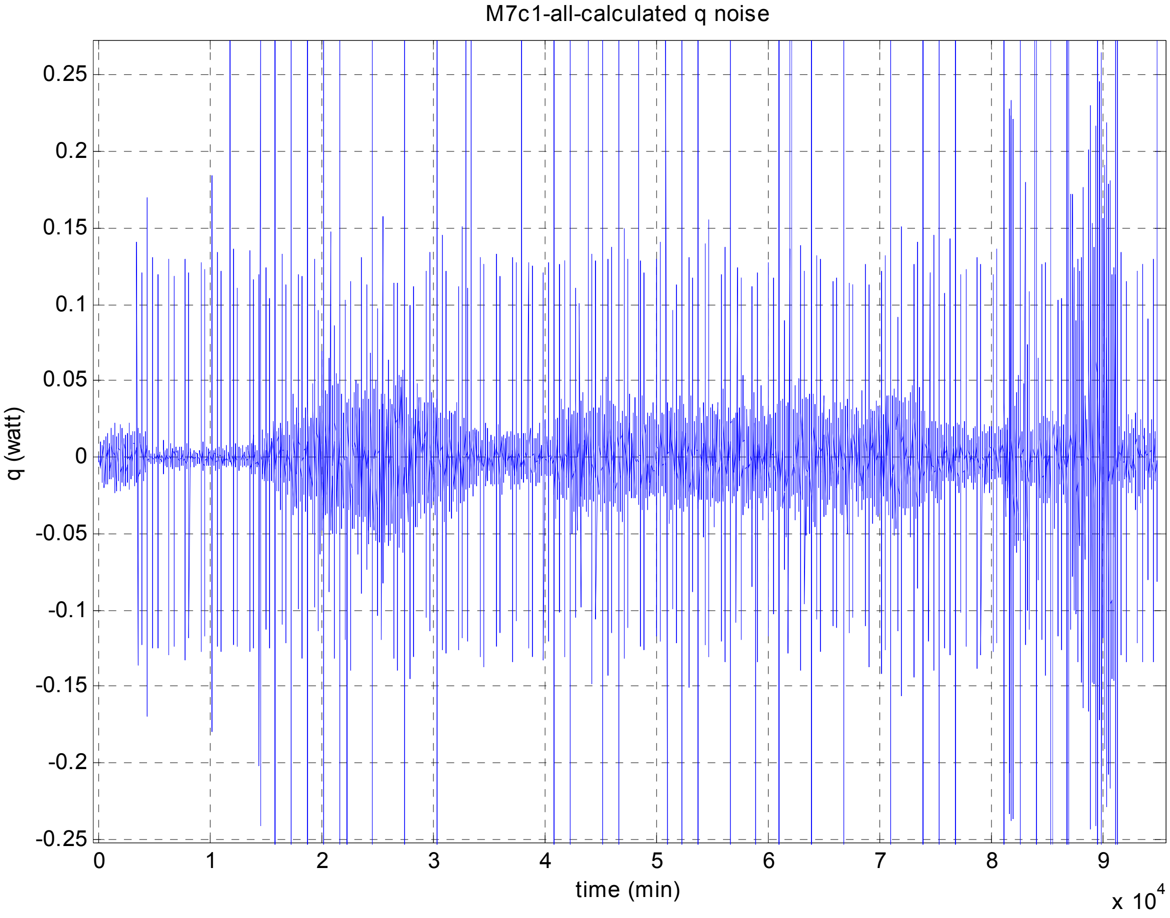

Fig 6. This shows the random noise in q when q is calculated point by point for M7c1_all. This noise is inherent in the data. Notice the large random noise in the last part of the run, due to large current noise. Thermistor and voltage fluctuations (the latter due to bubbling) are a main cause of the noise. Reasons for details in shapes are unknown at present. Shapes change from run to run as shown in following figures.

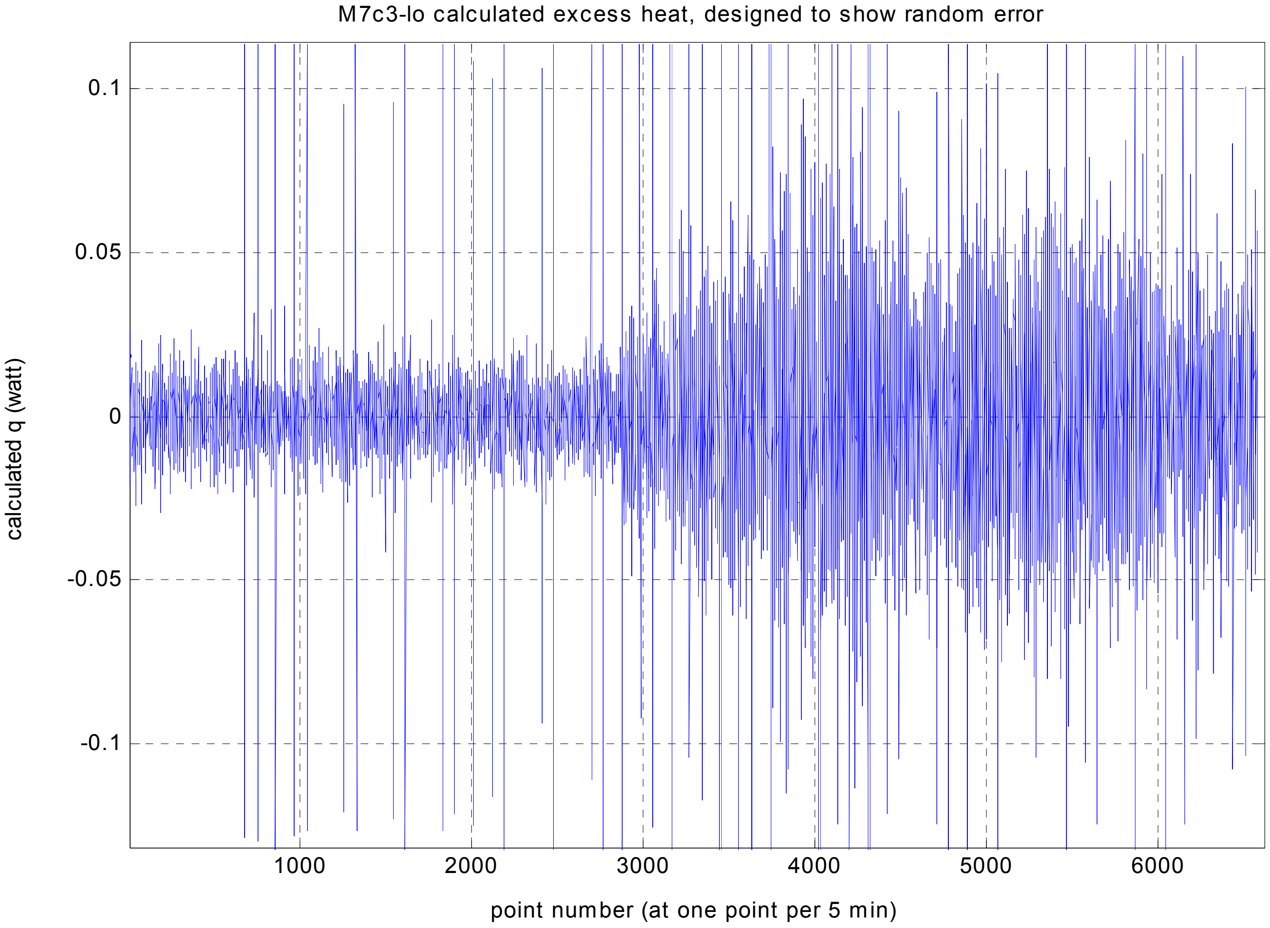

Fig 7. Calculated q noise for data of M7c3—lo. Here the inherent noise is low and constant for the beginning low current region (below pt 3000).

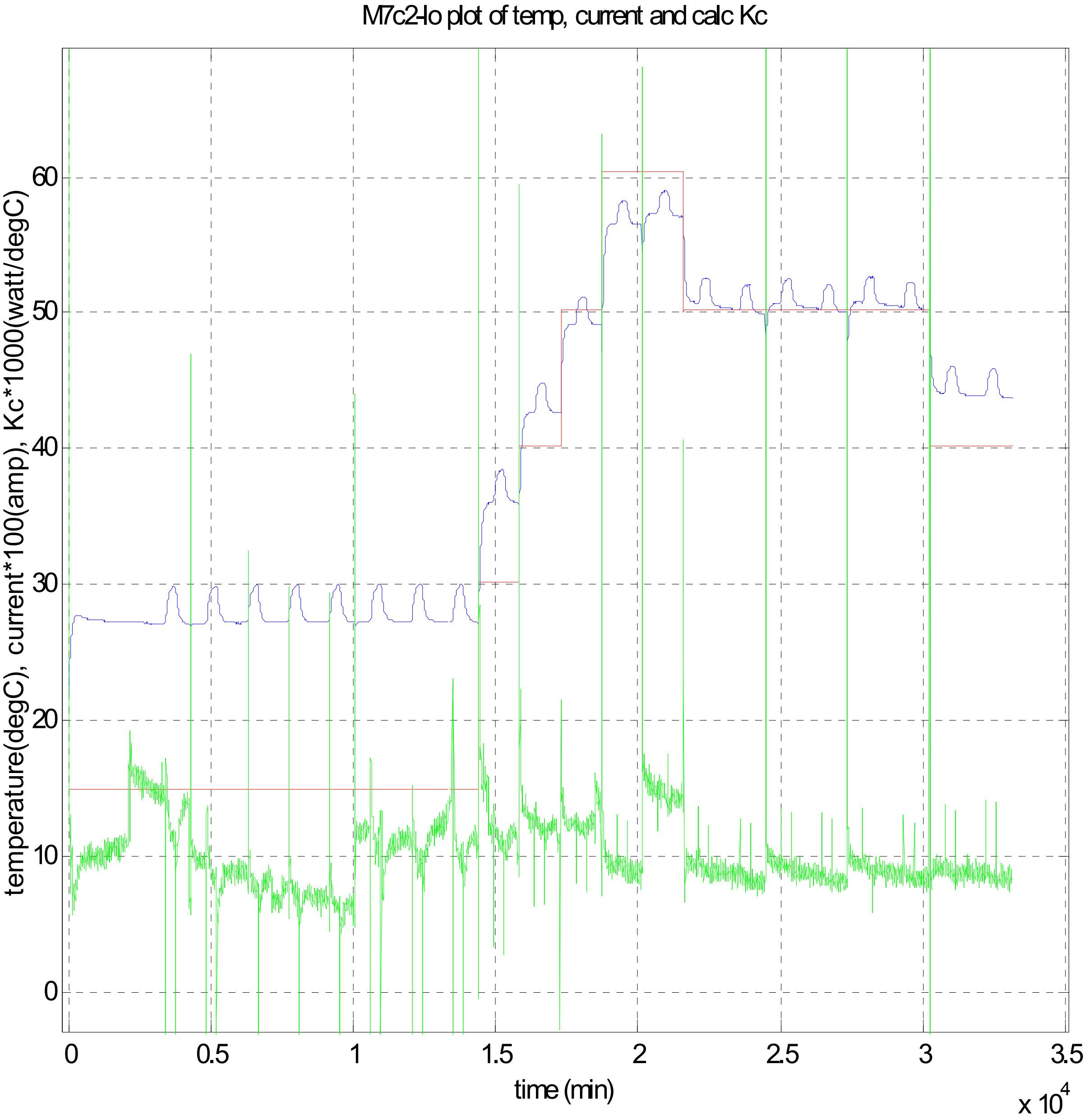

Fig 8. The temperature and Kc of M7c2—lo. The calculated Kc curve is anomalous and unacceptable. It looks normal beyond 22000 min, except for being low. Analysis shows that this could be caused by an excess heat pattern or an error in the calibration heat pulse.

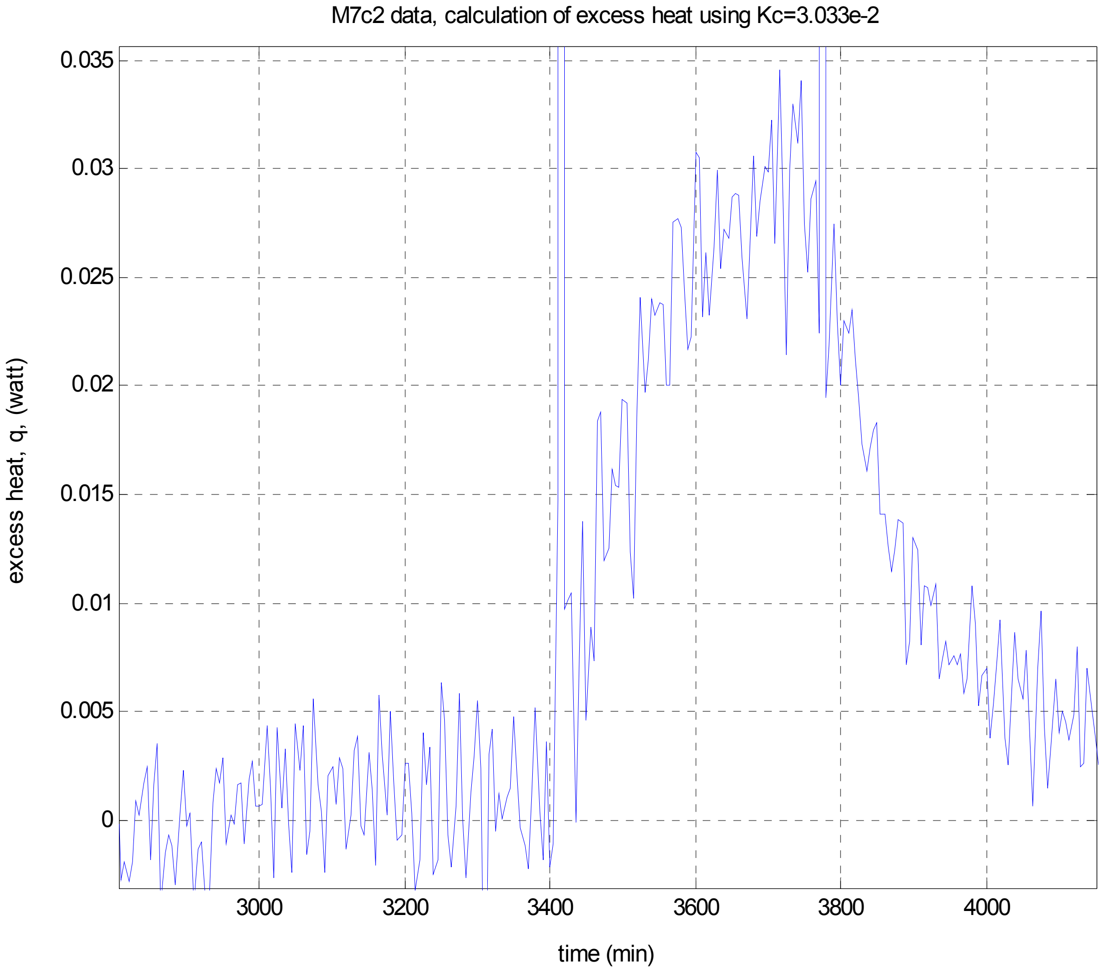

Fig 9. Calculated excess heat for the first heat pulse region of M7c2—lo, assuming a Kc the same as found for cell M7c1 for the same region and conditions.

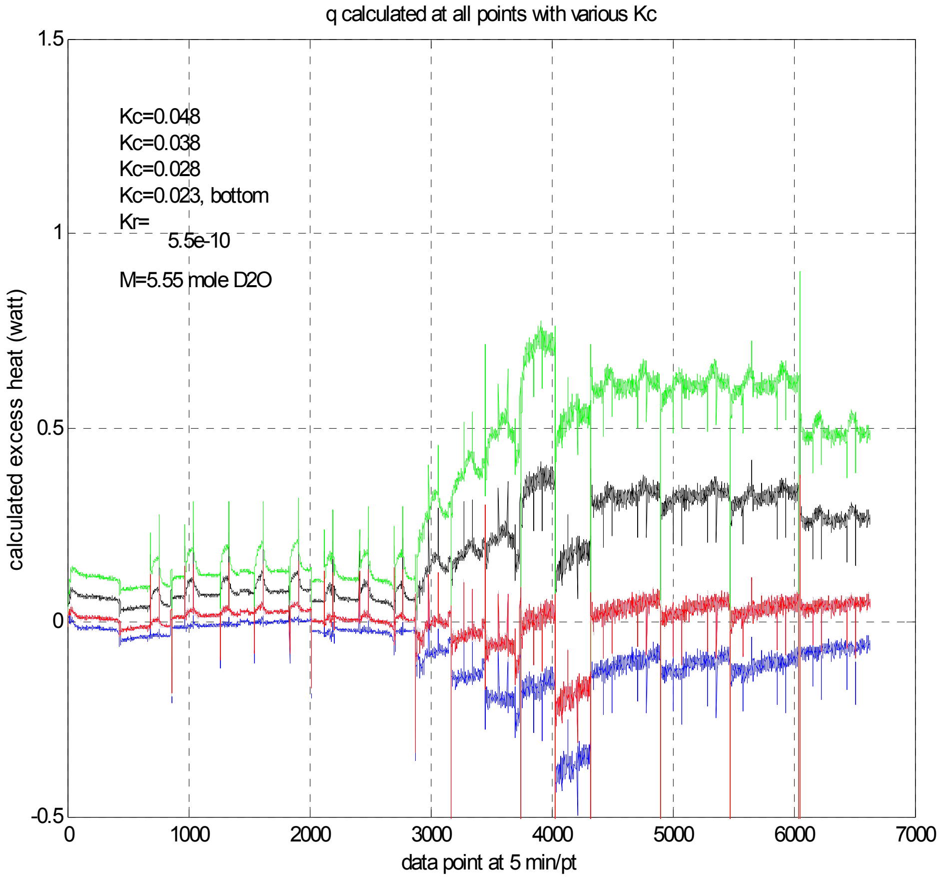

Fig 10. Cell M7c2—lo, q at all points using various Kc and M as 5.5 mole D2O equivalent. The real q curve is calculated to be between the red and black curves, but a systematic error in the magnitude of the heat pulses could explain the excess heat, and something like overfilling could explain the large q drops near 400, 2000, and 4000 points.