

# A ZERO GRADIENT CALORIMETER FOR THE MEASUREMENT OF ANOMALOUS HEAT FROM THE ELECTROLYSIS OF DEUTERATED METALS

Lee John Droege and Thomas F. Droege

1715 Karlann Drive, Black Hawk, CO 80422  
2 S. 942 Thornecrest La., Batavia, IL 60510

## ABSTRACT

A null balance calorimeter has been designed for the measurement of anomalous heat in electrolytic cells containing deuterium and palladium. Early measurements indicate an accuracy of less than 1% of the total energy processed through the calorimeter. Anomalous heat has been observed at the 4% level for palladium cathodes, or 4w per cc. Measurements have been made of cathode material resistance change and cathode gas absorption during electrolysis. Cell voltage variations over time have been correlated with cell gas evolution. Attempts have been made to correlate radiation with cell activity.

## INTRODUCTION

The announcement of Fleischmann and Pons [1] brought great excitement. Here was an experiment that amateurs could perform in their basement. No single discipline appeared to have an advantage. After many excited telephone calls between brothers in Colorado and Illinois, it was decided that our goal was to be the first to hold the land speed record for a "cold fusion" powered car. Since we are engineers, we planned to attack the problem of optimizing palladium cells for high power output. The approach was to design a sensitive calorimeter. Sensitivity was desired so that small improvements could be detected as we searched for optimum palladium conformations including intentionally rifted structures along various crystal planes [2]. Some time was spent searching for an old float zone refiner (Pfann) to make single crystal Palladium. But the machines we had used in the past all seem to have made it to the junk yard for their stainless steel weight as little as two weeks ahead of us. Eventually this effort

was abandoned and it was decided to use readily available numismatic palladium. By the time construction work started it was obvious that neutron measurements would be difficult, so even though one of us had some skill in nuclear instrumentation this further confirmed our selection of heat as the primary measurement.

Video tapes of the Santa Fe conference [3] were obtained and provided great help in designing the experiment. The debates over re-combination of hydrogen and oxygen, and how to take into account the refrigeration effects seemed to be more suitable to monks, angels and pins. A completely sealed cell with a catalyst was designed to avoid these arguments.

We believe that it is often very helpful to hear of other's mistakes and disasters. We report a few of ours here. We believe that the dry impartial style of technical papers prevents young people from discovering the joy of research. We consciously allow our excitement to show while attempting to report objectively.

## DESIGN

### Calorimeter Design

Early criticism of the technique of Fleischmann and Pons made it desirable to avoid heat flow measurements which depended on Newton's law of cooling, stirring, and thermometers. A Peltier thermoelectric cooler (TEC) had been recently purchased from a surplus house because it looked like a fun toy for experimentation. A quick experiment determined that it would be possible to use this device to build a calorimeter which would avoid the defects which had been so heavily criticized. The

design uses two concentric copper shells (Figure 1) both of which are held at the same constant temperature by analog computer driven power amplifiers. The outside of each shell is insulated with 1 1/2" of foam. The inner shell contains a single window in the foam insulation where a thermoelectric cooler (TEC1) connects it to the outside shell through blocks of aluminum. The design effort was to control

Our tests have shown that a constant current through a TEC with both faces at the same temperature produces a constant heat flow through the device.

Since the two shells are controlled to the same operating temperature to 10 millidegrees RMS, heat leaks between the inner and outer shell are reduced. The heat path through TEC1 is significant since TECs are not only heat pumps, but also thermal conductors. We have measured the thermal resistance to be 2.85 degrees Celsius per watt. Heat conduction through the TEC is compensated by placing a sensitive solid state thermometer (T1 and T2 of Figure 1) on each side of the TEC and making appropriate corrections to the heat balance computation.

The sensitive electronics is located in the constant temperature environment between the inner and outer shell. Circuits in this space are selected for constant heat dissipation. The current shunt for the between shells TEC1 is also located in this space. Temperatures are measured with the AD590 integrated circuit temperature sensor [4]. Analog circuits use the OP270 [5] for high stability and the OPA404 [6] for moderate stability and low leakage where circuits require long time constants. Very high stability of the sensitive circuits is assured through operating the OP270 amplifiers, which feature less than 0.6 microvolt per degree Celsius offset drift, in an environment which is maintained within 50 millidegrees of its set point. Our tests have confirmed that the balancing heater maintains its precision over the operating power range. This heater is composed of 40 metal film resistors selected in value for a best temperature coefficient. The assembly temperature coefficient has been measured at 17 ppm per degree Celsius. Resistance change at the operating point has been tested by operating at full power, then quickly removing the drive and measuring the resistance change. Checks over time have confirmed stability.

The configuration is not optimum. There are temperature gradients in both the inner and outer shell. There is typically 30 degrees Celsius rise between T1 and T3 of Figure 1 when operating at a 6 watt cell power. The test cell must discharge heat through convection. This produces a very long time constant of 1 1/2 hours which is

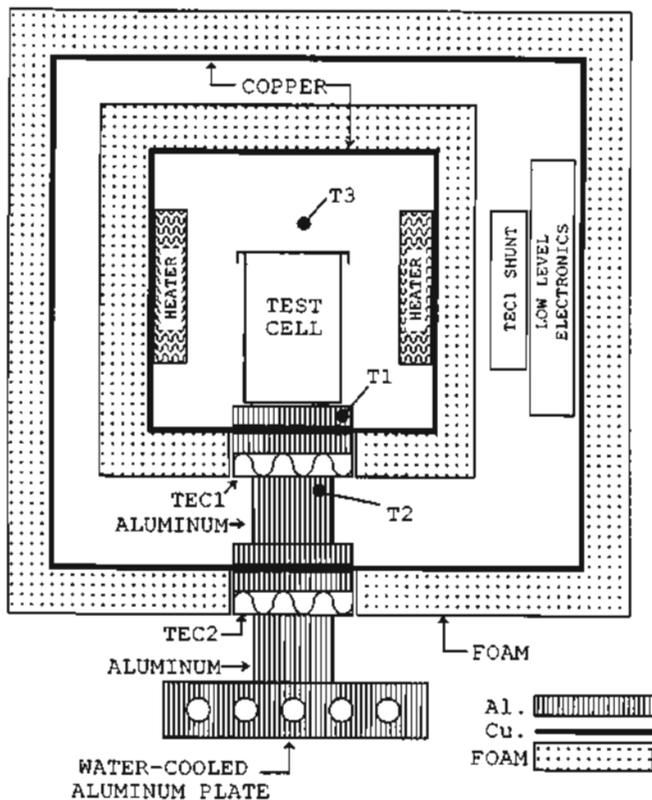


Figure 1. Calorimeter Layout. The calorimeter consists of an inner and outer copper shell heavily insulated with foam. Thermal electric coolers move heat between the shells and from the outer shell to a heat sink. Solid state thermometers control electronics to maintain both shells at the same temperature. The electronics reduces drive to the balance heater in the inner shell to compensate for heat added by the test cell.

the heat path so that all heat would be forced to flow through TEC1.

The outer shell is held at a computer-controlled temperature by connection through a second set of TECs to a water cooled plate. The TEC connecting the inner shell to the outer shell is driven by a precision constant current. The inner shell temperature is controlled to match the outer shell temperature by driving a distributed precision balancing heater glued to the inner wall of the inner shell.

a nuisance when performing calibrations. This also prevents measurement of the fine time structure of the anomalous heat when running 100 hour cell tests. By the time the tops of the shells are cut off and formed into plugs for access, there are many opportunities for errors in heat flow.

## Cell Design

Cells are built into 4 oz. polypropylene jars, Figure 2(a). The top contains 30 grams of Engelhard Catalyst D in the form of small cylinders. The catalyst is arranged so that the evolved gas has an extended path to the output pipe and recombined water is returned to the bottom of the cell.

The anode is wound on glass rods which are compression fit into teflon washers, Figure 2(b). Two layers are wound. The inner layer is the anode, the outer layer is used as a "dummy" as described below. The cathode is prepared as in Figure 2(c). The Palladium anodes are fabricated from slices of a one ounce Engelhard 99.9% Palladium bar purchased from a numismatic dealer. The slices are then turned on a small lathe until approximately round. Primitive equipment, limited skill, and the nasty machining properties of the coin palladium assure that no two cathodes are alike. Two holes are drilled in each end of the cathode by breaking numerous #80 drills. Platinum wires are inserted, and the cathode ends are squeezed in a vice. This cold welds the wires which are then operated in the Kelvin connection for the measurement of cathode resistance. Support structures are fabricated from polypropylene mesh, spot welded with a temperature controlled soldering iron.

Electrolyte is prepared by adding Lithium metal degreased with perchlorethylene to either Deuterium oxide, 99.9% atom% D, Aldrich Chemical Co. or ACS ultra pure water. The amount added is determined by weight after observing the solvent evaporation on a scale. The operation is carried out in very dry mountain air, at 9300 ft, but no special precautions are taken to prevent contamination.

A wide variety of cell configurations have been used as different fabrication techniques were tried. A typical cell contains 70 grams of electrolyte, 30 grams of catalyst, a 2mm by 25mm Palladium cathode, and sufficient .25mm Platinum anode wire to achieve a 5 to 1 anode to cathode area ratio.

## Gas System

The cell is vented outside the calorimeter through sections of 1/16" dia. stainless

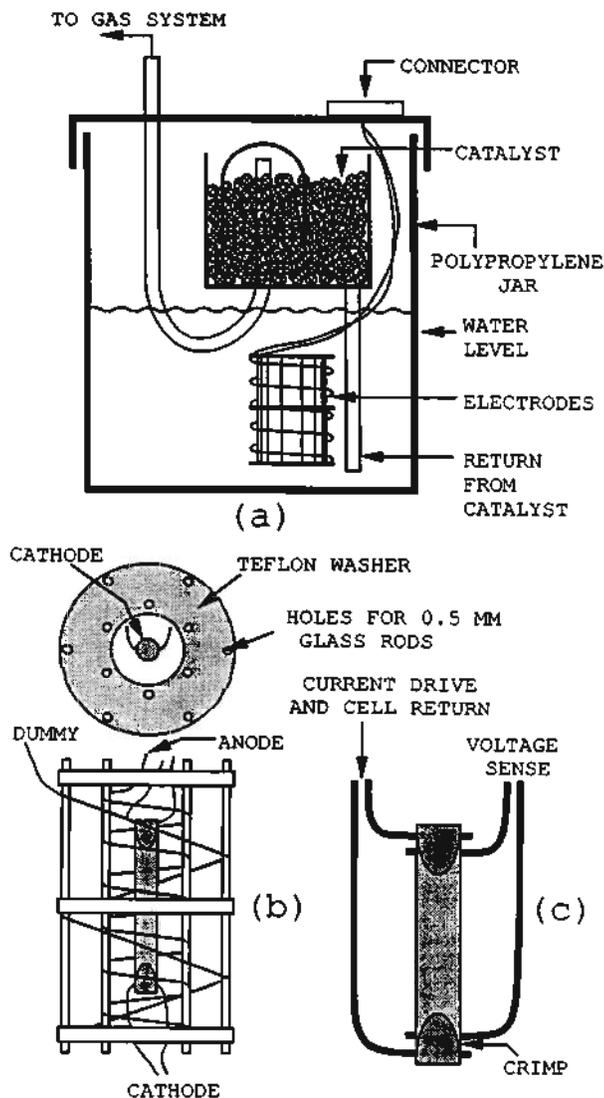
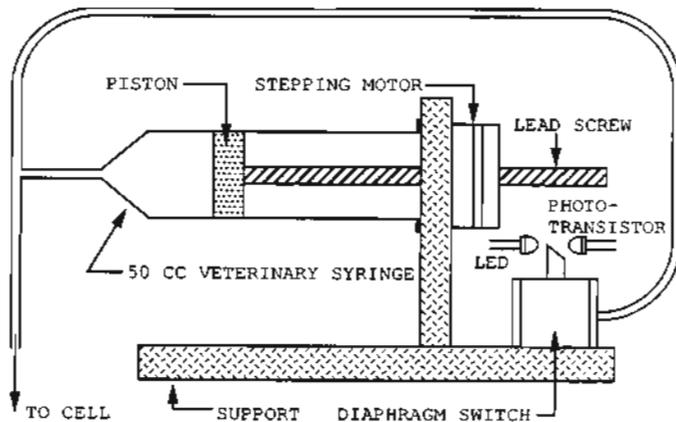


Figure 2. Cell Construction. a)Overall Cell Layout. b)Electrode Detail. c)Cathode Lead Connections.

Many unexpected things contribute small amounts of heat in the inner shell. Lead and connector losses must be considered at a level unusual in electronic design. While many of these problems have been found and cured, many others have been identified but are not correctable in this design. These details are far more limiting to the accuracy than the stability of the scheme. We are thus quite optimistic that future designs will achieve much greater accuracy.

steel tubing interconnected with PVC tubing. Figure 3 shows the gas measurement system. Gas from the cell is connected to



**Figure 3. Gas Measurement Servo** Pressure from the gas released by the test cell moves a latex rubber diaphragm with an attached flag. The flag moves between the light emitting diode and the photo transistor of a common solid state limit switch. The photo transistor output is read by an analog to digital converter and used to control a stepping motor connected to the piston of a large syringe. The piston is driven to restore the diaphragm position. A computer program measures the gas released by counting the steps required to maintain the balance.

a diaphragm switch and to a 50 cc disposable syringe obtained from a veterinarian. A metal vane is glued to the 0.006" latex rubber diaphragm. The vane is arranged to pass between a solid state limit switch of the type used to locate the home position for computer printers. This device contains a light source and a photodiode. It is normally connected to digital logic to give a beam interrupted signal. The device used gives full on to full off signals for about 0.002" travel. For this application the photodiode is read with the 12 bit precision data system. This allows resolution of a micro-inch of diaphragm travel. The vane position is sensed periodically by a computer program. The program controls a stepping motor with an internally threaded armature which drives a lead screw connected to the syringe piston. Each step displaces 0.014 cc of gas. By noting the direction of travel, varying the step rate in proportion to the error, and backing up to always close the error from the same direction, gas volume is measured to within one step. Hysteresis loop tests have confirmed this precision. A water manometer has been used to determine that pressure changes from

ambient are less than our measurement accuracy, which is 1/20" of water. Absolute accuracy is dependent on temperature and barometric pressure for which no corrections are made. The experiment is operated below grade in a residential basement where the temperature has been constant to within 2 degrees Celsius during most runs.

We operate the gas system in two modes. The normal mode measures the gas evolved from the electrolytic cell. This is measured to a precision of 0.014 cc. The normal volume measurement limit is the 50 cc syringe capacity. This can be extended by withdrawing gas into additional syringes with some loss of accuracy. For small gas changes, the system can be operated open loop and the evolved gas measured by the photodiode signal. This mode has a precision of 0.062 micro liters, a peak to peak noise level of 0.5 micro liters, and a range of +/- 62 micro liters. To observe small changes, the system is first operated in the closed loop mode to set the sense switch to the middle of its range. The loop is then opened and measurements are attempted before the system drifts off scale.

#### Radiation Measurement System

The primary radiation detector is a 1" National Radac NaI(Tl) crystal and RCA6199 photomultiplier tube. Both were purchased in 1954 and surprisingly survived prospecting for Uranium in the Mojave desert and 36 years in the junk box during an uncountable number of moves. A radium test source was secured from a second hand store for \$2 by searching a pile of broken watches for one that glowed in the dark. An earlier attempt for a source used ore from the mine in Colorado which supplied Mme. Curie. Unfortunately, this proved not to be radioactive. High voltage is provided by a high stability circuit similar to those used in high energy physics experiments [7]. The photomultiplier signal is amplified by a low noise J-FET amplifier similar to those used in high energy physics calorimeters [8]. The amplifier output is differentiated, discriminated, and pulse shaped before counting. The photomultiplier voltage is set as high as possible in an attempt to detect single photons associated with soft x-rays. This results in a majority of the counts being

due to photomultiplier tube noise.

The NaI(Tl) counter is placed above and outside the calorimeter. Its position is such that it is 7" away from the working electrodes. There is 0.040" of copper, 3" of plastic foam, 3/4" of catalyst, and approximately 1" of electrolyte between the cell electrodes and the detector.

#### Data collection system

An inexpensive (\$295) data system card was purchased and installed in an 80286 based personal computer for control of the experiment. The analog measurement section consists of an 8/1 CMOS multiplexer circuit, a sample and hold amplifier, and a 12 bit analog to digital converter. The measurement is bi-polar providing 11 bit precision. The card also contains three 16 bit counters and a digital I/O channel.

A second electronics card was designed for this experiment and is located in the space between the two calorimeter shells. The electronics in this location is selected for constant power dissipation. The constant temperature environment assures minimal problems from precision resistor and amplifier drift. The experiment is controlled by four 14 bit digital to analog converters (DAC) located on this card. These are loaded by computer program. Once set, the DACs control the calorimeter through analog computer techniques allowing the digital computer to be turned on and off without affecting operation. An uninterruptable power supply is essential as neighborhood chipmunks like to chew on the distribution transformers.

To guard against false settings of the DACs over the long running times they are reloaded every ten minutes. The result of commands are also recorded independently. For example, the cell current is commanded to a particular value. This command value is read by one channel. The cell current as measured by a shunt is read through another channel. This allows continuous monitoring of the experiment to verify that it is actually running where commanded. More than once this has prevented calling a press conference.

A CMOS multiplexer assures that all channels have the same gain. A zero volt reference and a -5 volt reference are measured as a system accuracy check. Most

signals are measured differentially to reduce common mode and noise problems. 100 samples of each of 18 variables are taken during 20 seconds of each one minute time interval. Because of the limited storage capacity of the data collection system (floppy disks) means of this data are recorded each minute. Since the cell voltage and current are critical and can vary widely, their RMS values are computed and recorded.

## OPERATION

### Cell Preparation

Before placing in the calorimeter, a cell is subjected to a series of operating cycles designed to remove hydrogen which may have been diffused into the cathode, to prepare the cathode for charging, and to remove impurities from the system. The removal of hydrogen is encouraged by cycling gas in and out of the cathode [10].

A voltage versus current curve is first taken in both the forward and reverse connection. The cell is then operated reversed at several currents in the expected operating range. Hoare [13] suggests that this may prepare the cathode for charging by removing a blocking layer which can develop while exposed to hydrogen in the gas phase. This then continues for 10 to 20 hours as a continued attempt to remove absorbed hydrogen. The cell is then placed through 10 or more cycles alternating forward and reversed at different currents in the operating range. This is followed by operation with anode and cathode tied together as the anode with the "dummy" as the cathode. This operation starts at the highest operating current and is reduced to zero over about an hour. This technique is used by electroplaters to improve plating operations when their solutions no longer produce a bright finish. The process tends to cause impurities to be deposited on the dummy where they are held by a very small current. Appropriate control runs have not been made to verify this procedure; however, the long charging times reported by others for cathodes of similar size have not been observed. All cathodes have been cut from the same Engelhard 1 ounce numismatic bar. All cells have shown excess heat within a day of high current operation. This is inconclusive, however,

since no fresh cells have been prepared since the discovery that CO<sub>2</sub> diffusion into the cell was producing initial heat.

Another technique used in an attempt to remove hydrogen from a cathode is to operate it in the calorimeter under the control of a computer program which alternates between a high and low cell current. A typical program alternates between 0 and 500 ma per square cm on an eight minute cycle. This results in gas amounting to .2 D/Pd atomic ratio "breathing" in and out of the cathode during each cycle.

#### Calibration

Calibration is started by selecting an operating power point and temperature. Most of the work reported below was done at a calorimeter power level of 8.052 watts and cell base temperature (T<sub>1</sub> and T<sub>2</sub> of Figure 1) of 320 degrees Kelvin. The power point is determined by varying the current in the TEC and noting the power in the balance resistor. A cell which physically matches the test cells but which contains resistors in an oil bath is now inserted into the inner shell and operated at various currents. The calorimeter should come to a balance at each test current so that the E\*I power added into the inner shell by the test cell is matched by a reduction in E<sup>2</sup>/R power in the balance resistor. Through careful selection of the balance resistor, accurate calibration of shunts, and differential measurement of all voltages to reduce common mode errors, calibration of the power balance should be within 0.1%, or better. Since the time constant of the system is 1.5 hours, each calibration point requires 10 hours to settle to 0.1%.

Due to the pressure of actually making measurements on the phenomena, ultimate calibration was not pursued. Because the calorimeter was designed and built in two weeks, we did not have time to properly consider requirements, so the design did not couple the test cell tightly to the inner calorimeter shell. Better coupling would significantly reduce the time constant and make calibration faster. Since the phenomena was supposed to take weeks to appear, this was not considered to be important to the design.

It was a mistake not to build calibration

resistors into the cells. A second set of heater resistors should be added for future designs. The next design will allow using the Pt anode wire as a heater to allow calibration by inserting heat at the location where it is generated during operation. The moderate effort made to reduce common mode rejection and other measurement errors, proved not to be good enough. Summation of the elements contributing to the heat balance cannot be made to the desired 0.1% precision.

As experienced analog circuit designers, we are aware that the design requirements are quite difficult and require great care in planning and execution. Instrumentation amplifiers are essential. Each wire in the calorimeter has to be carefully designed for heat dissipation. The method and location of lead attachment for voltage measurement is critical. It is not safe to use connectors since they are apt to introduce uncontrolled heat.

#### Resistance Measurement

Every ten minutes, a current pulse is passed through the outer connections of the Palladium cathode (Figure 3c) to measure its resistance. This proved to be more difficult than expected. The four terminal Kelvin connection used normally solves problems measuring low value resistance. These cells have several added problems which have only approximate solutions. The cell operating current passes through the cathode. Depending on the grounding choice, this produces an end-to-end voltage which is measured as if it were the result of the test current. While the computer can be programmed to command the cell current to zero during the measurement, this does not appear to be wise from the view point of understanding cell operation. Further, there appear to be long term cathode end-to-end voltages which change during the measurement if the cell current is turned off. Measurements were taken by reading the cathode end-to-end voltage before and during the application of the test current. This would be acceptable if done fast enough. Unfortunately, the current driver was not designed for fast response time. Thus the one second pulse periods chosen for this design and the rather rapid cell voltage variations assure large errors. Measurements are taken at two current values to investigate cathode ionization.

## Cell Power Checks

At the Santa Fe meeting Richard Garwin [9] proposed that there might be a problem in accurately computing the power into an electrolytic cell. To check this, we compute the cell power two ways and record the ratio as a "Garwin" number. During the 20 second interval of each minute when the parameters are measured 100 samples of each are taken. Cell voltage and current are arranged to occupy adjacent channels of the 18 multiplexed readings so that they are measured as closely together as possible. The sequence is to scan through all channels then to repeat the scan 100 times in this same 20 second interval. Power is computed by taking the mean of the voltage readings and multiplying it by the mean of the current readings. Power is also computed by taking the product of the instantaneous readings and then taking the mean of these products. With either ideal constant voltage or constant current operation of the cell these computations are mathematically equivalent. However, with real current sources differences are possible. The ratio of these computations is recorded as the Garwin number and is used as an indication of the quality of the power measurement.

## EXPERIMENTAL RESULTS

We have operated this calorimeter about 5000 hours in a variety of experiments designed to survey cell operation in an attempt to find where interesting work might be performed. All data should be considered preliminary. We report results to indicate where we plan continued work.

### CO<sub>2</sub> Problems

About 3400 hours of experimental data was discarded as worthless after it was discovered that CO<sub>2</sub> had diffused into the cells through a water trap which served as a pressure relief. This would convert most of the cell lithium hydroxide to a lithium carbonate in about two weeks operation for what was thought to be a .1N cell (see below). The result was a gradual increase in cell voltage which eventually went beyond either the calorimeter power capacity or the voltage drive capacity of the servo. Fortunately the electrolyte from all the runs had been saved. Measurement indicated that most old cells

had a pH in the range of 7 to 9. All had started at a pH of 12.5 or higher as determined from reference samples. The last run made before this discovery was an H<sub>2</sub>O Pt-Pt cell filled with 1N LiOH. It appeared to show an "anomalous heat" level of 100 mw. This run was repeated after replacing the H<sub>2</sub>O in the safety trap with NaOH ("Easy Off" oven cleaner) which absorbs CO<sub>2</sub>. The "anomalous heat" disappeared and was then within the calorimeter error. The system has since been completely sealed, the water trap having been replaced with a "blow out" piston formed from a second syringe.

After the surprise finding of the CO<sub>2</sub> effect, we bought a pH meter and began to check cell pH. We found it lower than expected, and eventually found that the chain of our balance had come off its pivot at some unknown time. While the pH comparisons above are valid since we kept reference samples, we were working with lower pH electrolyte than planned since the scale problem produced low weights of Lithium. Because pan weights were needed for the 1N sample, it was near the expected value.

It is thought that CO<sub>2</sub> may be a more serious problem for the closed cell operation used here. With open cells the very large gas flow out of the cell may purge CO<sub>2</sub> from the cell to an acceptable level. The partial pressure dynamics of such a situation are unknown to us.

### Resistance Measurements

The history of cathode #9 is typical. This cathode is 2mm in diameter and 19mm long with 16 mm spacing between the inner measurement connections. The initial measurement of #9 was 300 micro-ohms. This increased to 600 micro-ohms after operating for 2 hours at 60 ma per square cm. See Figure 4. After 20 hours of operation the resistance had reached the 750 micro ohm range. There was then little change over a variety of operating currents during 1400 hours of runs with six changes of electrolyte. During long off periods, or electrolyte changes, the resistance would reduce to the vicinity of 600 micro-ohms. It never approached the initial value. Since gas content varied widely over the many runs after the initial charging, resistance measurement does not appear to be as valuable as we had hoped as an

indication of the cathode status.

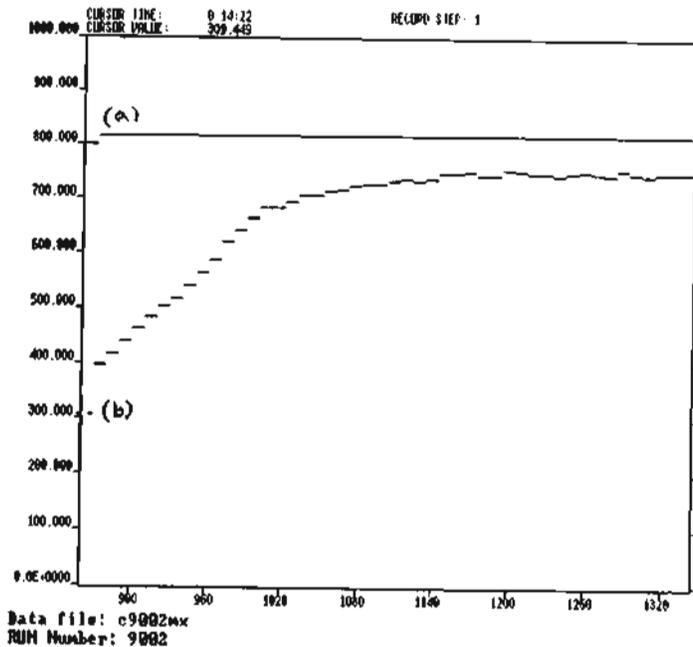


Figure 4. Cathode Resistance During Charging. The upper trace is cell current showing charging at 60ma per sq. cm. The lower trace is cathode resistance. The Vertical Scale is in micro-ohms with major divisions at 100 micro-ohm intervals. The Horizontal scale is in minutes with major divisions at one hour.

Resistance measurements are performed at .1 and 1 ampere. There is some indication that for very long electrolysis, the resistance is nonlinear. The lower current has been found to produce a higher resistance reading. This is consistent with an ionization process as reported by Moore [11].

#### Radiation measurement

Counts accumulated during each one minute time interval by the NaI(Tl) counter are recorded. Attempts have been made to correlate the radiation count with other experimental parameters.

A series of runs were made where the cell current was alternated between a high and low value with an eight minute period. Count rates were compared between the high and low current levels with no result. Other combinations were tried. Scaramuzzi[12] reported observation of neutrons on dynamically loading Titanium with deuterium. In an attempt to measure this, comparison was made between high, high going low, low, and low going high bin periods on the assumption that there would

be a different radiation pattern depending on the direction and rate of gas flow to the cathode. During these tests there was a cyclical gas change amounting to .1 D/Pd atomic ratio. There was nothing of statistical significance observed. Tests with a four hour period show a hint of a relation. The great length of time required to remove counter drifts has prevented a definitive experiment from being performed to date.

By watching the cell voltage variation with time and adding the radiation counter pulse to the cell voltage with the A+B feature of an oscilloscope, it is possible to imagine that there is often a radiation pulse at the cell voltage peak as might be the result of a fusion event causing a cell voltage change. Binning of radiation counts by cell voltage revealed nothing significant.

Tests were made with film wrapped around the cell during runs which displayed "anomalous heat." Development revealed darkened film with images of the absorber we had inserted between the cell and film. Control runs at the same temperature and with similar metal objects next to the film demonstrated that this was a temperature effect.

Electrolyte from a closed cell which had displayed "anomalous heat" was analyzed for tritium content. There was no difference between it and a reference sample.

We have binned all data accumulated so far on cells which indicate excess heat against the direction and quantity of gas flow during the one minute data interval. This reveals a small but persistent effect which indicates the possibility that there are slightly fewer counts in the detector during the one minute intervals in which a small amount of gas has left the cathode. The theory is that first something happens to produce heat. The heat causes some gas to leave the cathode. While gas is out of the cathode, fewer radiation events occur. This is not yet statistically significant.

#### Long term gas measurements

All the gas measurements are indirect. What is measured is gas which appears in the system. This is presumed to be the left over oxygen from the disassociated hydrogen or deuterium absorbed by the

Palladium. Due to limited resources we have not confirmed this by chemical analysis of gas samples. Figure 5 is a typical gas run. The dotted line indicates

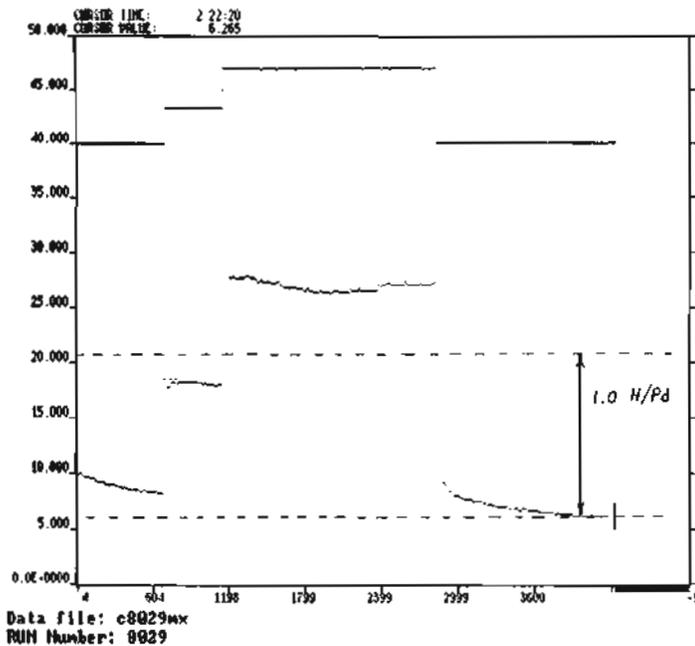


Figure 5. Gas Absorption by the Cathode for an H<sub>2</sub>O cell. The upper trace shows cell current starting at 500 ma per square cm, stepping to 1 amp per sq cm, then returning to zero. Lower trace is the gas absorbed by the cathode. The vertical scale is in cc with 5 cc major divisions. Dotted lines indicate gas for 1/1 H-Pd ratio. Horizontal axis is in minutes with major divisions at 10 hours.

gas change for 1.0 H/Pd atomic ratio. This cathode has been through many charging cycles so the initial content of gas is unknown. Because of the failure of the resistance to return to its initial value, it is believed to be non zero. Hoare [13] suggests it might be close to .6 H/Pd. This is cell #8 which has a cathode area of 0.686 square cm, and a volume of .0229 cc. The run starts with 11 hours of operation at zero current. During this time, the cell is outgassing due to previous operation on the bench. Note that the operation of the catalyst produces a reduction of gas volume for gas leaving the cathode. After applying .5 amp per square cm. the cathode quickly gains gas amounting to .7 H/Pd. Later application of 1 amp per square cm. pushes the increase of H/Pd to the area of 1.3. After removal of current the gas slowly returns to near the initial value though it is still outgassing after more than 20 hours. For cells showing anomalous heat there is a general trend, for example, Figure 11. The gas enters the

cathode quickly, particularly for cathodes which have undergone many current changes cycles. After the first few hours, the gas slowly decreases. After more time, there is a gradual increase in gas content, during which time there is displayed an apparent increase in anomalous power level.

### Short Term Gas Measurements

Figure 6 shows the changes of gas seen in Figure 5 to higher time resolution. The dots are at one minute intervals. Figure 6(a) shows first gas entry. Since this is

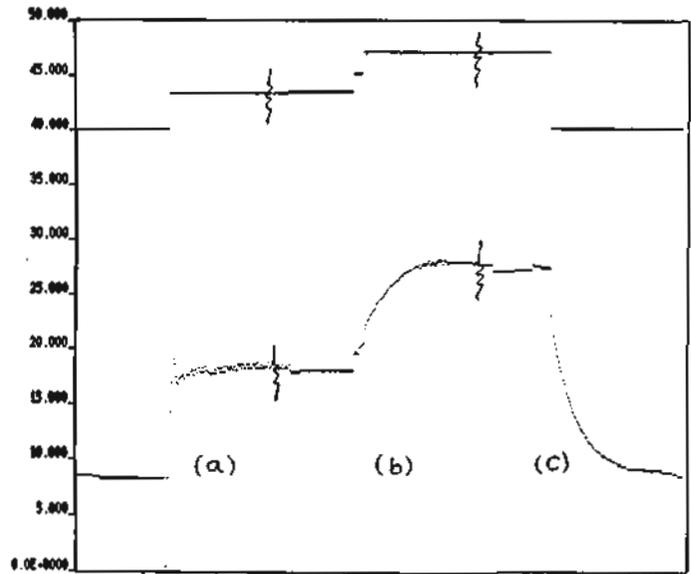


Figure 6. Detail of Cathode Gas Absorption Shown in Figure 5. Left section shows detail of turn on. Center section shows switching from .5 to 1 amp per square cm. Last section shows evolution of gas on current turn off. Vertical scale is in cc with major divisions at 5 cc. The curves are plotted with dots at one minute intervals.

a cathode that has a history of 28 previous runs totaling 598 hours, gas enters quickly. The overshoot at the beginning is presumably caused by the catalyst failing to recombine the gas at the evolution rate when it is cold. After a few minutes the recombination heat allows it to catch up. Later, when going to high current density, gas absorption is slower, Figure 6(b). Finally in Figure 6(c) the gas release on turn off is shown. About 20% of the gas is evolved during the first minute after current turn off. Estimating gas content by removing the cathode and weighing is difficult as it is not clear how to extrapolate back to time zero. The gas servo can be observed to be stepping within a second of the application or removal of

current.

### Voltage and Gas Observations

During calibration runs with resistors in oil, and H<sub>2</sub>O cell operation, the Garwin number is constant to a few parts in 10E6. This is well beyond the precision of the system and can only be explained by the averaging technique used. Thus for these runs it is easy to measure the power correctly.

Because Garwin prompted us to use our oscilloscope, we have observed that the cell voltage follows a saw tooth wave form. The data collection program has been arranged so that it can be interrupted briefly allowing a minute of "high speed" data taking. During this time cell voltage, current, radiation and gas are measured at .1 or .02 second intervals. Data is stored directly in memory to avoid errors caused by disk waits. For gas measurement, the servo is turned off and gas volume is measured by the relative position of the flag interrupting the photo diode.

03-11-1990 22:33:32 A:V9020RB

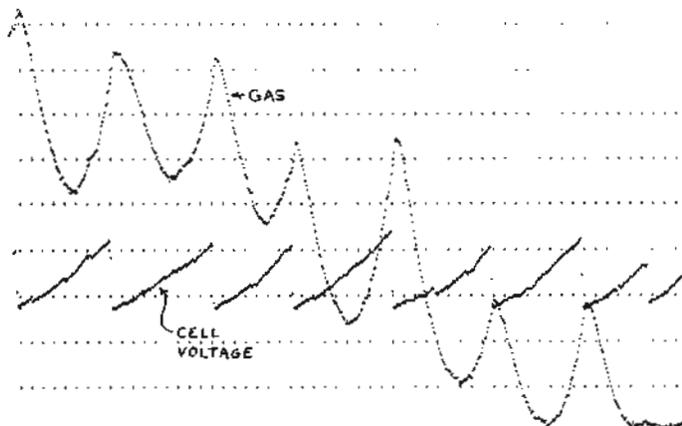


Figure 7. Cell Voltage and Gas Relationship The upper trace is the cell gas volume. The lower trace is the cell voltage. The vertical scale for the gas is 12.5 micro liters per major division. The vertical scale for the voltage is one volt per major division. The horizontal scale is one second per dot.

Figure 7(b) is the voltage waveform from a cell operated at 285 ma per square cm. We have observed that the frequency and amplitude of the cell voltage change with current density and cathode gas content. These measurements were taken with the cell driven from a constant current source. Cells operated with a constant voltage source display a current saw tooth.

For D<sub>2</sub>O runs which show "anomalous heat", the saw tooth wave form and the limited band width of the current source cause the Garwin number to show variations as large as 2 parts in 1000. The variation as observed is always in the same direction, the mean of the instantaneous products being smaller than the product of the means. As a conservative approach, the product of the means is used in the energy balance which tends to decrease the "anomalous heat" seen.

At first it was thought that the saw tooth wave form was caused by bubble formation and release at the anode producing a negative resistance. Visual observations do not confirm this.

We speculate that the cathode pulses as a surface film forms, becomes unstable like the heated earth's surface, and breaks off like a thermal bubble in the earth's atmosphere. During the process it seems likely that some compressed gas will also escape resulting in a cell gas volume increase. Whatever the source, the cell appears to alternate long periods, of order 1 to 60 seconds, of positive resistance with short periods, of order 50 milliseconds, of negative resistance. It is not surprising that a relaxation oscillation occurs under these conditions.

Figure 7 shows simultaneous measurements of the cell voltage 7(b) and gas volume 7(a). Each time the cell voltage drops, the gas volume starts to decrease. Because of the complexity introduced by the catalyst, it is not entirely obvious whether this is a gas release or absorption by the cathode. Since there is a hint of a gas release pulse just before the gas decreases, gas release is favored. This will be clarified by further study.

The saw tooth waveform is seen with D<sub>2</sub>O Pt-Pd cells and is not seen with H<sub>2</sub>O Pt-Pt cells. The status of H<sub>2</sub>O Pt-Pd cells has not been resolved.

### Calorimeter Calibration

We wish to stress that we are running a completely closed system. Much of the early criticism of Fleischmann and Pons' work was concerned with estimates of energy that left the cell with the disassociated gas. Those problems are avoided here. All runs end with the cell at the same

condition as it was when the run began. Differences, if any, relate to the amount of gas that remains absorbed in the palladium cathode.

All of the curves except the heat balance are printed directly from the raw data. For the heat balance, a single set of calibration constants has been computed from a calibration run and is used throughout. In addition, a factor for the thermoelectric cooler is computed for each run from the period when the cell is operated at zero current. When observing the energy balance curves, the reader should keep in mind that they are the differences between numbers which are many times the size of the displayed scale range.

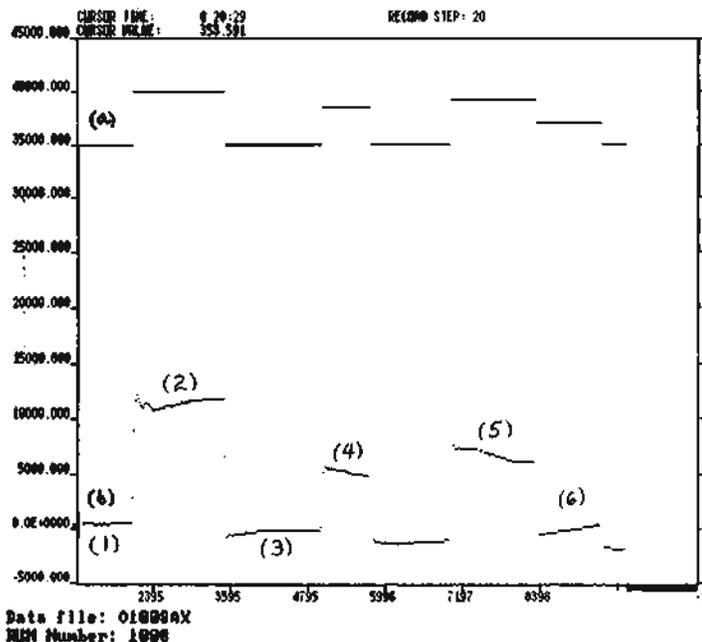


Figure 8. Calibration Run Using a Resistor Cell Filled with Oil. The upper trace is the cell current. Currents start at zero. Successive current values are .5, .35, .43, and .2 amperes. The lower trace is the energy balance in joules. The vertical axis is in joules with major divisions of 5000 joules. The horizontal axis is in minutes with major divisions of 20 hours.

Figure 8 is a typical 141 hour calibration run. Here a cell of the same shape as the test cells is filled with oil and power resistors.

The cell was allowed to come to the calorimeter temperature for 8 hours before data taking started. Data starts with a 17 hour period (1) where the cell is operated

at zero current. The bottom curve is the net power into the cell in joules. Positive on the curve indicates that more energy has been put into the calorimeter shell than has been taken from it.

During the 23 hour period (2) the cell was operated at 500 ma. During the transition, the calorimeter accumulates heat. A perfect design would not do this, but this design contains a better conduction path through lower specific heat copper for the heaters. Thus when the primary source of heat transfers from the heaters to the test cell, the copper shell gets only slightly cooler. The cell on the other hand, transfers heat mostly by convection so that it gets much hotter and so causes a net accumulation of heat in the calorimeter shell.

The whole process reverses at (3) when the cell current is commanded back to zero. In order to return exactly to zero, the  $I \cdot I \cdot R$  computation of the heater power must track exactly the  $E \cdot I$  computation of the cell power. This can be guaranteed at one operating power point if things are stable by picking calibration constants. To assure that the computation is correct when the test cell operates at a different power point than the calibration cell, calibration is done at several points, (4), (5)... A curve is then fit for the best calibration.

This curve is then used for a set of H<sub>2</sub>O and D<sub>2</sub>O test cells. For this calibration, a balance was maintained over 141 hours to 2 kilo-joules out of a total of 4 mega-joules which passed through the calorimeter. This represents a drift of 4 mw. A more practical measure is the worst drift rate during the run caused by imperfect compensation at the various operating points. This is somewhat less than 20 mw for the above run. We do not have enough runs to compute any meaningful statistics for the calorimeter drift rate. We have measured the worst drift observed for a calibration run which otherwise appeared to function correctly. This is 50 mw.

#### H<sub>2</sub>O Runs

Figure 9 shows the operation of an H<sub>2</sub>O cell. The run consisted of 11 hrs at zero current, 35 hrs. at 500 ma. per square cm, and 22 hrs at zero current. Figure 9(a) is

the current. Figure 9(b) shows the voltage which slowly increases from 5.2 to 5.8 volts during the run. Because the voltage is slowly increasing, the temperature above the cell, Figure 9(c), slowly increases by 1 degree Celsius during the run. This

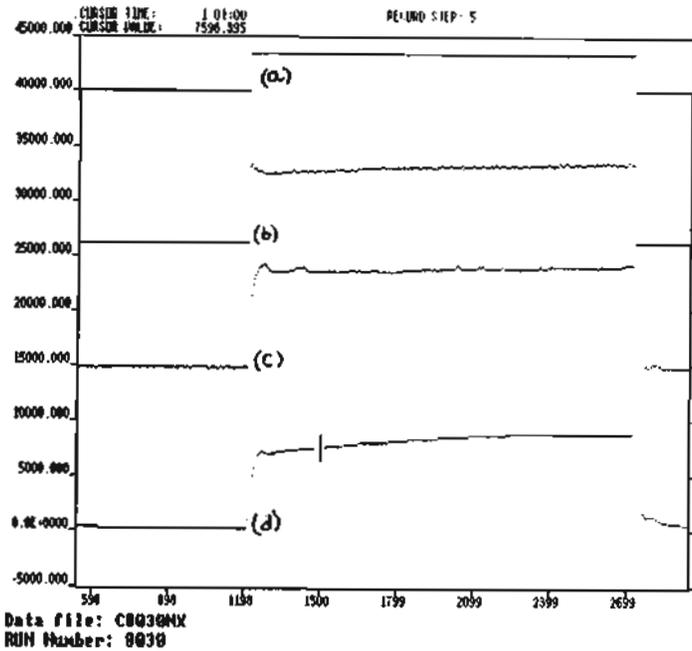


Figure 9. H2O Cell Operation Trace a) is the cell current of 500 ma per square cm. Trace b) is the cell voltage. Trace c) is the temperature above the cell. Trace d) is the energy balance. The vertical scale is energy in joules. Major divisions are 5000 joules. The horizontal axis is in minutes with major divisions at 5 hours.

results in the net energy curve, Figure 9(d) slowly increasing as the cell contents get hotter. When the current is removed, the net energy curve returns to zero as the contents of the cell return to the initial temperature. For this run, energy drift has been removed to illustrate the energy balance.

### D2O Runs

Figure 10 is the energy balance for a D2O cell which shows "anomalous heat". We show drift range on this curve representing the worst drift observed during oil and H2O cell runs. Since the aforementioned CO2 problems ruined many calibration runs the six or so remaining do not provide meaningful statistics. This was the 19th run for this cell but the first since a change of electrolyte where the cell was open and exposed to the air for about 1 hour. After current is applied there is a

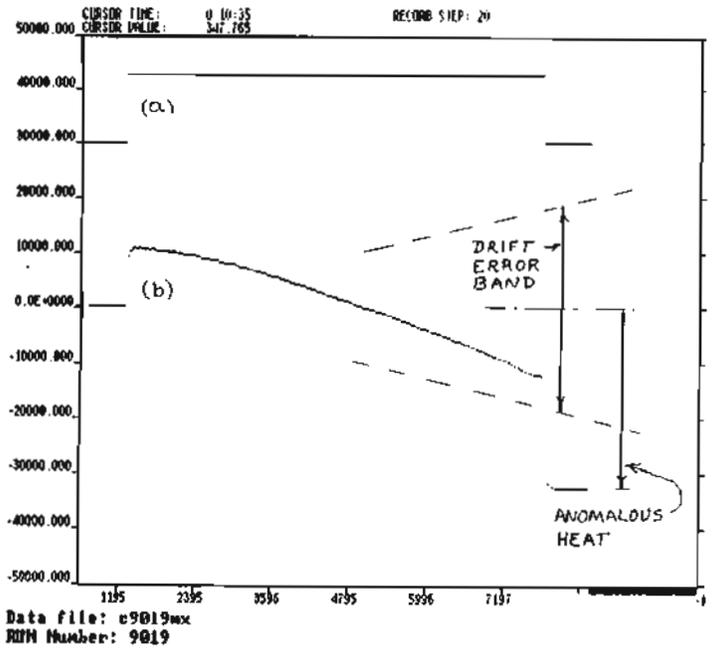


Figure 10. D2O Cell Operation The upper trace (a) is the charging current of .46 amps per sq. cm. The lower trace shows the net energy during the run. The vertical scale is energy in joules with major divisions at 10,000 joules. The horizontal scale is in minutes with major divisions at 20 hours. Dotted lines indicate the largest drift observed.

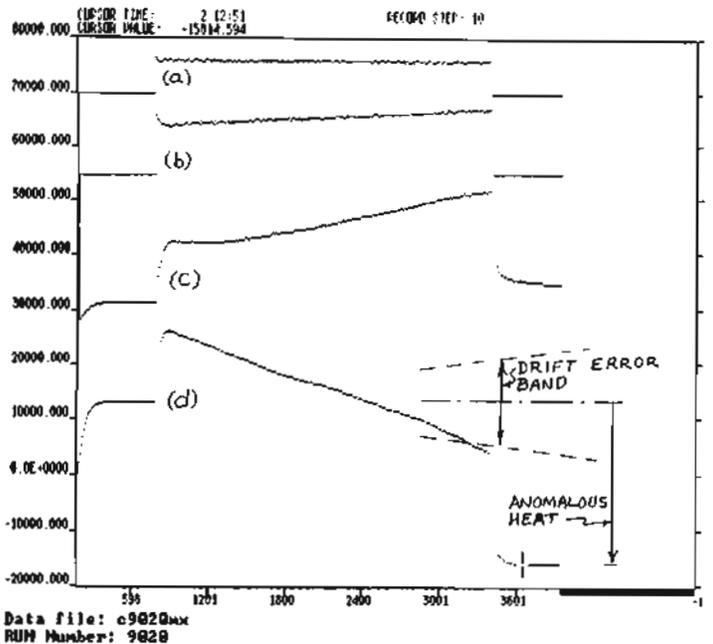


Figure 11. D2O Cell Operation The upper trace (a) is the charging current of .46 amps per sq. cm. Trace (b) is the cell voltage. Trace (c) is the gas volume. Trace (d) is the net energy during the run. The vertical scale is energy in joules with major divisions at 10,000 joules. The horizontal scale is in minutes with major divisions at 20 hours. Dotted lines indicate the largest drift observed.

period of about 15 hours during which the cell maintains an approximate heat balance.

The balance then changes in the direction of "anomalous heat" with a gradual acceleration during the run. Towards the end of the run, "anomalous heat" is being produced at nearly twice the maximum probable drift rate. We do not see this change of slope on the H2O or oil runs.

Examination of the detail of D2O cell operation, Figure 12(e), shows that there are alternating periods of heat release and balanced operation. There is some suggestion that the gas system is more active when heat is being produced. Comparison of a D2O run showing "anomalous heat" Figure 12, with an H2O run Figure 13,

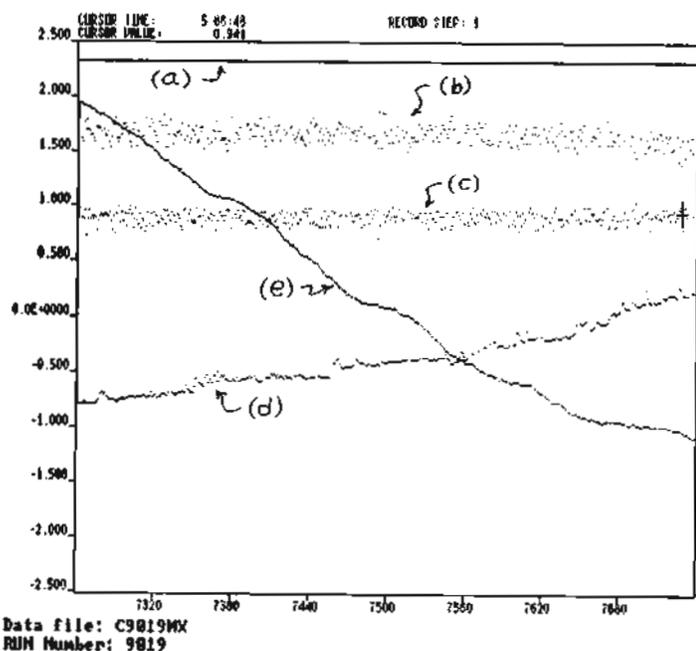


Figure 12. D2O Cell Operation Detail The upper trace (a) is the charging current. Trace (b) is the Garwin number variation. Trace (c) is the RMS cell voltage. Trace (d) is the gas volume. Trace (e) is the energy balance. The vertical scale is the RMS cell voltage. The horizontal scale is in minutes with major divisions at one hour. All scales are the same as for Figure 13.

indicates that the gas system is more active, the RMS cell voltage is higher, and the Garwin number is farther from one. Figure 12 and 13 use the same scales for the various variables. Unfortunately, because the cell of figure 13 used a 1mm dia. cathode vs 2mm for the cell of Figure 12, a direct comparison cannot be made. We show this comparison because other data indicate that there may be valid differences. The great length of time required for runs and the availability of

only a single calorimeter preclude the completion of the obvious experiments.

Between D2O run C9019 (Figure 10) and D2O run c9020 (Figure 11) an H2O calibration run, C8030 (Figure 9) was performed. This run indicated a calorimeter drift of 33 mw which was removed from the elthalpy curve for the purpose indicated. This drift happened to be in the direction of "anomalous heat", however other H2O runs have drifted in random directions. There followed run C9020 which accumulated 29,064 joules during a 2,612 minute run for an average "anomalous heat" of 185 mw. Run C9020 shows an increasing heat release which averages about three times the estimate of maximum drift from the various calibration runs. This data is representative of the last 2000 hours of calorimeter operation where we have alternated D2O runs with oil or H2O calibration runs. These runs are ongoing and continue to show similar results.

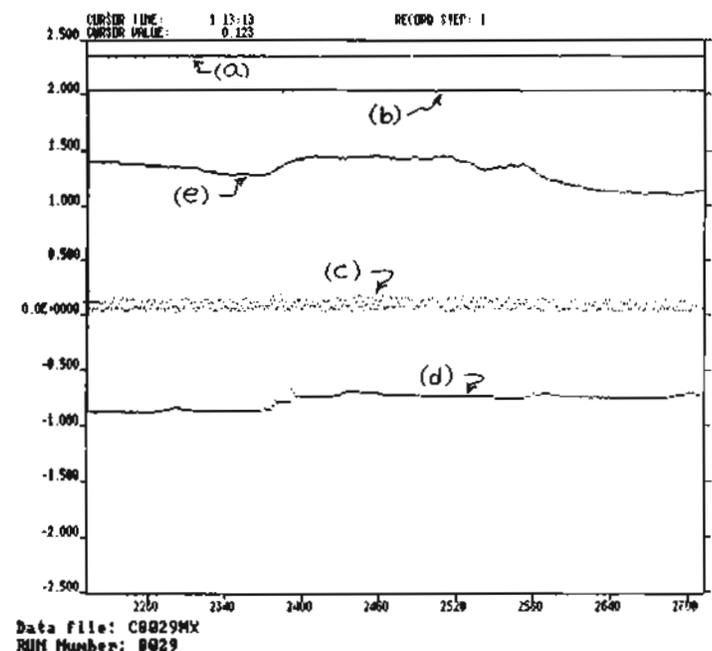


Figure 13. H2O Cell Operation Detail The upper trace (a) is the charging current. Trace (b) is the Garwin number variation. Trace (c) is the RMS cell voltage. Trace (d) is the gas volume. Trace (e) is the energy balance. The vertical scale is the RMS cell voltage. The horizontal scale is in minutes with major divisions at one hour. All scales are the same as for Figure 12.

## DISCUSSION

We find the evidence for "anomalous heat" to be persuasive but not absolutely convincing. We have presented data that we

believe to be representative. Still, there are enough calibration runs which show too much heat and D2O runs which show little or no heat that the whole process could be noise. We present our willingness to continue work without financial support as a measure of our conviction. We continue to see differences between D2O and H2O cells which indicate that something is happening beyond normal chemistry.

Once we are at an operating point, we have not observed calibration data which indicates a change in drift rate of more than a few mw. We therefore consider runs such as C9019, Figure 11, to be highly significant. We can only conclude that something is changing in the cell to cause it to increase in heat output.

While the calorimeter concept is very promising, the current implementation produces a different calorimeter every time we open it up to change cells. The 50 mw drift rate claimed is believed to be conservative, even for our string and glue construction. There is every indication that this can be reduced to the area of 1 mw when it is rebuilt to allow reassembly to a constant configuration.

Garwin was correct in advising caution in the measurement of cell power. The saw tooth wave form is subject to measurement error if proper technique is not used.

The resistance measurements indicate that the change to the beta phase occurs rather quickly. As the material is exercised it stays at high resistance, indicating that considerable gas remains in the material. The cathode accepts gas long after the beta transition appears to be complete, indicating that gas may be going into the "rifts in the slip planes" [11] as described by Moore.

The use of cell preparation seems to speed up the appearance of "anomalous heat." We have not yet done a proper control experiment. Ultra clean procedures do not appear to be required to observe "anomalous heat." However, our observations are about a factor of five below other reports. The materials used, except D2O, were of commercial quality. We did not discover the CO2 problem until working together over Christmas, so all the cells operated to date contain lithium carbonate encrustations which have accumulated over

several electrolyte changes.

We have just begun to learn how to make these measurements. We understand how to do almost everything an order of magnitude better. It is a pleasure to work where there appear to be endless interesting possibilities to be explored. While we have not yet climbed into the drivers seat of our fusion car, we could not be having more fun.

#### ACKNOWLEDGEMENT

We thank Charles A. Nelson, Jr., Ming-Jen Yang, and Dick Gustafson for physics advice and review. We particularly thank Charlie Nelson for always finding an ordinary explanation for our 30 sigma effects. (We could kill him.) We thank Ming-Jen Yang for computer analysis software. Dick Gustafson and Moyses Kuchnir provided useful stuff. Merle Watson is thanked for building the electronics and for being an enthusiastic spectator. Gary Drake is thanked for the amplifier design and simulation of the calorimeter. Thanks to Rick Mouche' for appearing with pH paper at a crucial time and for teaching one of us a little chemistry. Douglas R. O. Morrison is thanked for integrating the field with his "Cold Fusion Notes". Last, we thank the USA tax system for supplying a significant portion of our expenses.

#### REFERENCES

- [1] M. Fleischmann, S. Pons, and M. Hawkins, *J. Electroanal. Chem.* 261,301-308 (1989).
- [2] G.A. Moore, Dissertation. Princeton, (1939).
- [3] Workshop on Cold Fusion Phenomena, *Los Alamos Video Tape*, Santa Fe, (1989)
- [4] AD590 Data Sheet, Analog Devices, Inc.
- [5] OP-270 Data Sheet, Precision Monolithics, Inc.
- [6] OPA404 Data Sheet, Burr-Brown Corp.
- [7] United States Patent #4,888,763
- [8] G. Drake et. al., *IEEE Nuclear Science Symp.*, San Francisco (1985).
- [9] *ibid.*, Workshop, Day 2 Discussion.
- [10] T. B. Flanagan and F. A. Lewis, *J. Electrochem. Soc.*, 108,473 (1961)
- [11] *ibid.*, Moore, 91
- [12] *ibid.*, Workshop
- [13] J. P. Hoare, *J. Electrochem. Soc.*, 107,635 (1960)