Review of the calorimetry of Fleischmann and Pons

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LENR-CANR.org

August 2020

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Abstract

This is an introduction to the calorimetry in experiments by Fleischmann and Pons. From 1989 to 1993, they published a series of papers describing three methods of calorimetry: isoperibolic, phase change and a cooling curve analysis. These experiments culminated in boil-off experiments in which cells produced over 100 W of excess heat, and stayed hot for hours without input power. In 1996, Pons reported another series of experiments in which reactions up to 101 W were sustained continuously for up to 70 days with reflux calorimeters.

This introduction is for the general reader. It includes definitions of the isoperibolic, phase change and other methods, a discussion of how calibrations are performed, and some of the advanced features of Fleischmann and Pons' equipment and methods.

Some skeptics claim that their calorimetry was unreliable or controversial. Some of the skeptics' objections are reviewed.

Calorimetry is at the heart of this experiment

A calorimeter is an instrument that measures heat. Calorimetry, encompassing various different methods of measuring heat, is vital to the study of cold fusion.

Why is calorimetry so important? Because, as Fleischmann said, "heat is the principal signature of the reaction." If you do not detect heat, there is probably no cold fusion reaction. The principal nuclear product of cold fusion is helium. The amount of helium is small, and difficult to detect. [1] Cold fusion seldom produces radioactivity.

This is totally unlike plasma fusion. A plasma fusion reaction that produced as much heat as a typical cold fusion experiment would also produce so much penetrating radiation it would kill an unshielded observer. So, it is millions of times easier to confirm with a radiation detector than

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[1] Fusing 1 g of deuterium in a D-D reaction produces 345,000 MJ of heat. Helium has been confirmed in several studies. This is challenging, because there is such a tiny amount of helium, and because helium is ubiquitous in the atmosphere.

with a calorimeter. This was the first objection raised by skeptics, and it remains the most common one. It is discussed below.

Heat is also the most important aspect of cold fusion because it is the proof that the reaction is nuclear, rather than chemical. This heat is called "excess heat" or "excess enthalpy" because with the electrochemical technique, there is usually some input power, and output heat exceeds the input. Although in some cases, there is no input power and only output heat.

As Fleischmann and Pons pointed out in their first paper, the reaction produces far more energy per gram than any chemical reaction:

> Enthalpy generation can exceed 10 W cm^{-3} of the palladium electrode; this is maintained for experiment times in excess of 120 h, during which typically heat in excess of 4 MJ cm^{-3} of electrode volume was liberated. It is inconceivable that this could be due to anything but nuclear processes. [1]

Gasoline produces the most heat of any common chemical, 0.034 MJ/cm^3. [2] In other words, the first reported cold fusion experiments produced 118 times more heat than any chemical fuel of the same volume. [3] Subsequent experiments produced up to ~300 MJ, which is ~10,000 times more energy than any chemical reaction, or roughly as much heat as you would get if you burned the whole table the experiment sits on. [4] Not only does cold fusion produce vastly more heat than a chemical reaction, there is no chemical fuel in the cell, and no chemical changes take place, other than forming palladium deuteride when the experiment begins, which has only negligible potential energy.

Some critics have claimed that measuring heat is not a valid way to detect a nuclear reaction. This is incorrect. These people are used to the modern method of using a particle detector. They have forgotten that radioactivity was first explored with calorimetry. Martin Fleischmann pointed out that the Curies and others first showed that the heat from radium cannot be chemical because it exceeds the limits of chemistry, and because there are no chemical changes in the radium. Marie Curie described how it produces heat and no detectable chemical or physical changes:

> Radium possesses the remarkable property of liberating heat spontaneously and continuously. A solid salt of radium develops a quantity of heat such that for each gram of radium contained in the salt there is an emission of one hundred calories per hour. Expressed differently, radium can melt in an hour its weight in ice. When we reflect that radium acts in this manner continuously, we are amazed at the amount of heat produced, for it can be explained by no known chemical reaction. The radium remains apparently unchanged. If,

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[2] This is ignoring the oxygen needed to burn the gasoline, which lowers the energy per cubic centimeter. Gasoline produces 44 MJ/kg, and the density is 0.78 g/cm^3. It produces almost as much energy per gram as exotic rocket fuels, which are the most energy-dense chemicals yet devised.

[3] Cold fusion produces even more measured by mass, but this is complicated. The palladium does not take part in the reaction. It is unchanged. The deuterium in it fuses to form helium, and as noted above the best estimate is that it produces the same amount of heat as plasma fusion: 345,000 MJ/g. The point is, a very small object produces far more heat than any chemical reaction could. It resembles a match that burns for weeks.

[4] Not quite the whole table. Ref. [5] describes an experiment that produced 294 MJ over 158 days. This is the heat produced by burning 29 kg of wood. A wooden laboratory table weighs about 36 kg.

then, we assume that it undergoes a transformation, we must therefore conclude that the change is extremely slow; in an hour it is impossible to detect a change by any known methods.

As a result of its emission of heat, radium always possesses a higher temperature than its surroundings. This fact may be established by means of a thermometer, if care is taken to prevent the radium from losing heat. – Century Magazine, 1904 [5]

Calorimetry is also an important subject to understand when doing cold fusion because the calorimeter itself is an integral part of the experiment. It plays a role, enhancing the reaction or inhibiting it. A bulk palladium electrochemical cold fusion experiment depends upon having the right kind of palladium material, preparing it correctly, and loading it with deuterium to a high level of concentration. [2] If you master these things and you succeed in triggering a reaction, you can often boost it by raising the temperature. You need a calorimeter designed for the purpose, that allows a higher temperature. Some types, especially isothermal ones, will work to keep the temperature from rising, thus inhibiting the reaction. This also inhibits positive feedback, which Fleischmann and Pons think is important.

Four Methods of Calorimetry

In their initial experiments, Fleischmann and Pons used isoperibolic calorimetry, which is described in detail below.

Later, they did a series of experiments in which excess heat gradually appeared over the first two or three weeks of the test. After the heat is well-established, electrolysis power is increased. This heats up the cathode and triggers much higher heat, which causes the water in the cell to boil-off in about 20 minutes, leaving the cell dry. During these tests, they used three methods of calorimetry:

1. Isoperibolic before the boil-off.

2. Phase change calorimetry when the water boiled away.

3. Cooling curve analysis after the boil-off.

Years later, Pons developed an isoperibolic reflux calorimeter with continuous boiling.

Fleischmann and Pons discussed these methods in many papers. For isoperibolic calorimetry:

Ref. [3] Fleischmann, M., et al., *Calorimetry of the palladium-deuterium-heavy water system*. J. Electroanal. Chem., 1990. 287: p. 293.

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[5] "Melt in an hour its weight in ice" means phase-change ice calorimetry. I assume this is how Curie determined the energy was 100 cal/hour per gram of radium. 100 cal/hour is 0.116 W. Their sample was 0.129 g of radium chloride ($RaCl_2$), which is 76% radium by weight (0.1 g of radium), so it is producing 12 mW. I assume Curie observed it melts ~0.1 g of ice per hour, which is 33 J, or 33 J/3600 s = 0.009 W (9 mW). Skeptics sometimes claim that such milliwatt levels of heat cannot be measured, but no one in 1898 and no one today doubts that the Curies and other competent scientists can measure this with confidence. Granted, cold fusion heat is often on top of input power, but input power can be measured with great precision, and subtracted.

The phase change boil-off experiments are described here:

Ref. [4]. Fleischmann, M. and S. Pons, *Calorimetry of the Pd-D$_2$O system: from simplicity via complications to simplicity.* Phys. Lett. A, 1993. **176**: p. 118 [6]

A detailed look at the cooling curve method used after the boil-off is here:

Ref. [5]. Pons, S. and M. Fleischmann. *Heat After Death. in Fourth International Conference on Cold Fusion*. 1993. Lahaina, Maui: Electric Power Research Institute 3412 Hillview Ave., Palo Alto, CA 94304

The isoperibolic continuous boiling reflux calorimeter is described here:

Ref. [6]. Roulette, T., J. Roulette, and S. Pons. *Results of ICARUS 9 Experiments Run at IMRA Europe*. in *Sixth International Conference on Cold Fusion, Progress in New Hydrogen Energy*. 1996. Lake Toya, Hokkaido, Japan: New Energy and Industrial Technology Development Organization, Tokyo Institute of Technology, Tokyo, Japan.

"Reflux" means the water vapor is cooled, condensed back into water, and it falls back into the cell.

Isoperibolic calorimetry used in phase 1

Fleischmann and Pons used mainly isoperibolic calorimetry. In the first approximation, this method is easy to understand when it is applied to a stable reaction in a narrow range of temperatures. The reader is warned that Fleischmann and Pons used it in a much more difficult, complicated reaction. They had good reasons for doing this.

An isoperibolic calorimeter is typically a cell (a test tube) filled with water. Figure 1 shows the Icarus System cell developed by Fleischmann and Pons in the IMRA laboratory in France. Fleischmann delivered one of these cells to the New Hydrogen Energy (NHE) laboratory in Sapporo, Japan, along with detailed instructions for how to use it. Miles was later a visiting researcher at this lab, and he used this cell in an experiment. The results were analyzed by Miles, Fleischmann and Imam. [7-9]

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[6] The version of the paper linked to here was published in the ICCF-3 proceedings. The text was the same as the Phys. Lett. A version.
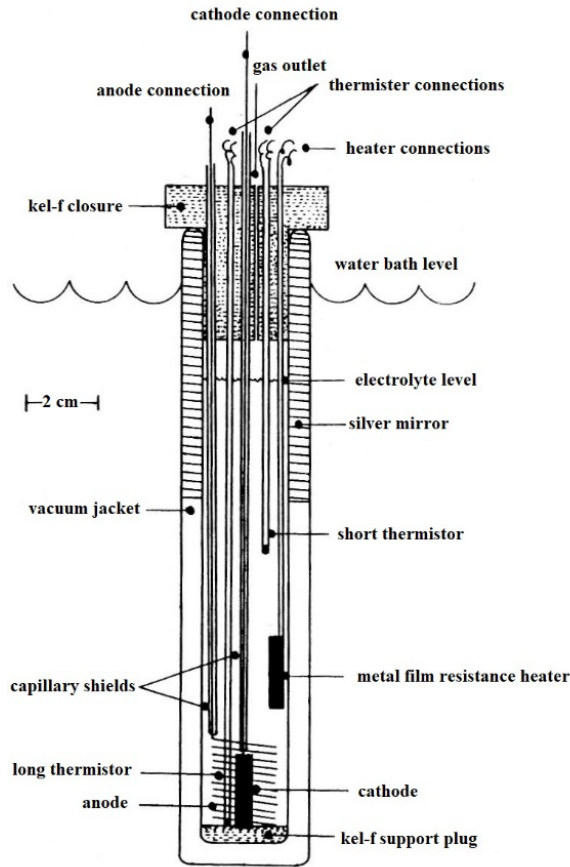
Figure 1. ICARUS-2 isoperibolic calorimeter cell used by Fleischmann and Pons. It has a silvered mirror inside the vacuum jacket at the top, and clear glass at the bottom. Diagram approximately to scale. Figure from Ref. [10]

To measure heat, you begin by calibrating. You put an electric heater in the cell, turn it on to a fixed power level, and see what temperature the cell reaches. Later, you put a palladium cathode in heavy water electrolyte. You look to see whether the cell becomes hotter than it did at the same power level during calibration. If it does, it is producing excess heat from cold fusion. The cell is usually placed in a constant temperature water bath, or in some cases left in temperature-controlled air. Fleischmann and Pons often calibrated with what they called "blank" tests, that is to say, control tests with electrolysis using platinum electrodes in heavy water. [11] Platinum cannot produce cold fusion.

Figure 3 shows data from a rudimentary calorimeter. This is a test tube (a cell) cooled in ambient air. In the test tube is water, a resistance heater, and a thermistor. (See Appendix A.) The cell and the ambient air start at the same temperature. The heater is turned on with 1.1 W of power. The temperature of the water in the cell rises until it plateaus and remains stable, about 140 minutes into the test. It stabilizes 4.5°C warmer than ambient air (right axis). At 200 minutes, power is increased to 1.7 W. By 270 minutes the temperature in the cell has risen 7.2°C higher than the ambient air.
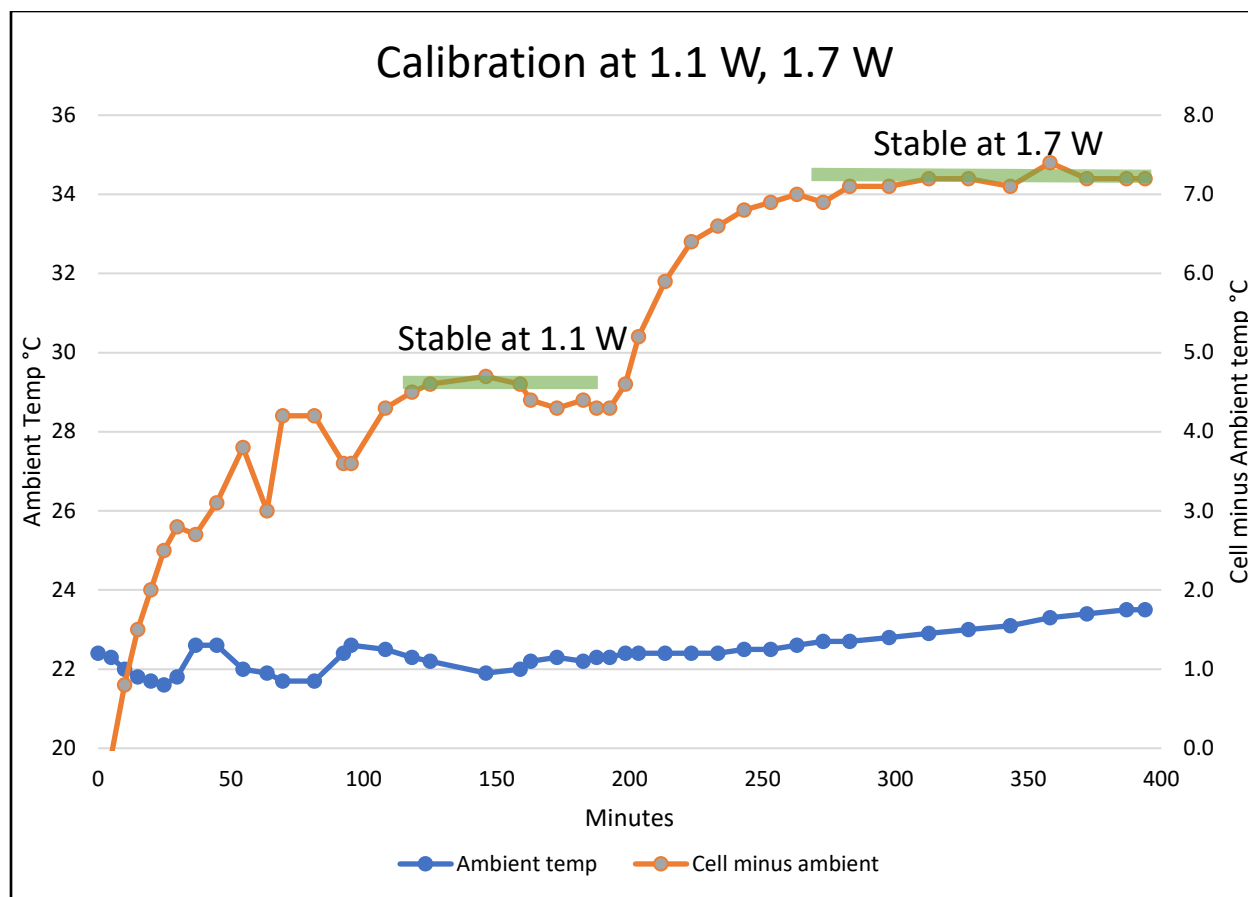
Figure 2. A simulation of 19th century conditions. Calibrations at 1.1 W and 1.7 W, in a rudimentary calorimeter in uncontrolled ambient air.

The stable temperature differences of 4.5°C and 7.2°C are calibration points. They are added to a calibration curve (Figure 3), along with three other points from other tests. The calibration curve should be linear and it should intercept the axes at the origin (0, 0). Otherwise, something is wrong with the calorimeter.
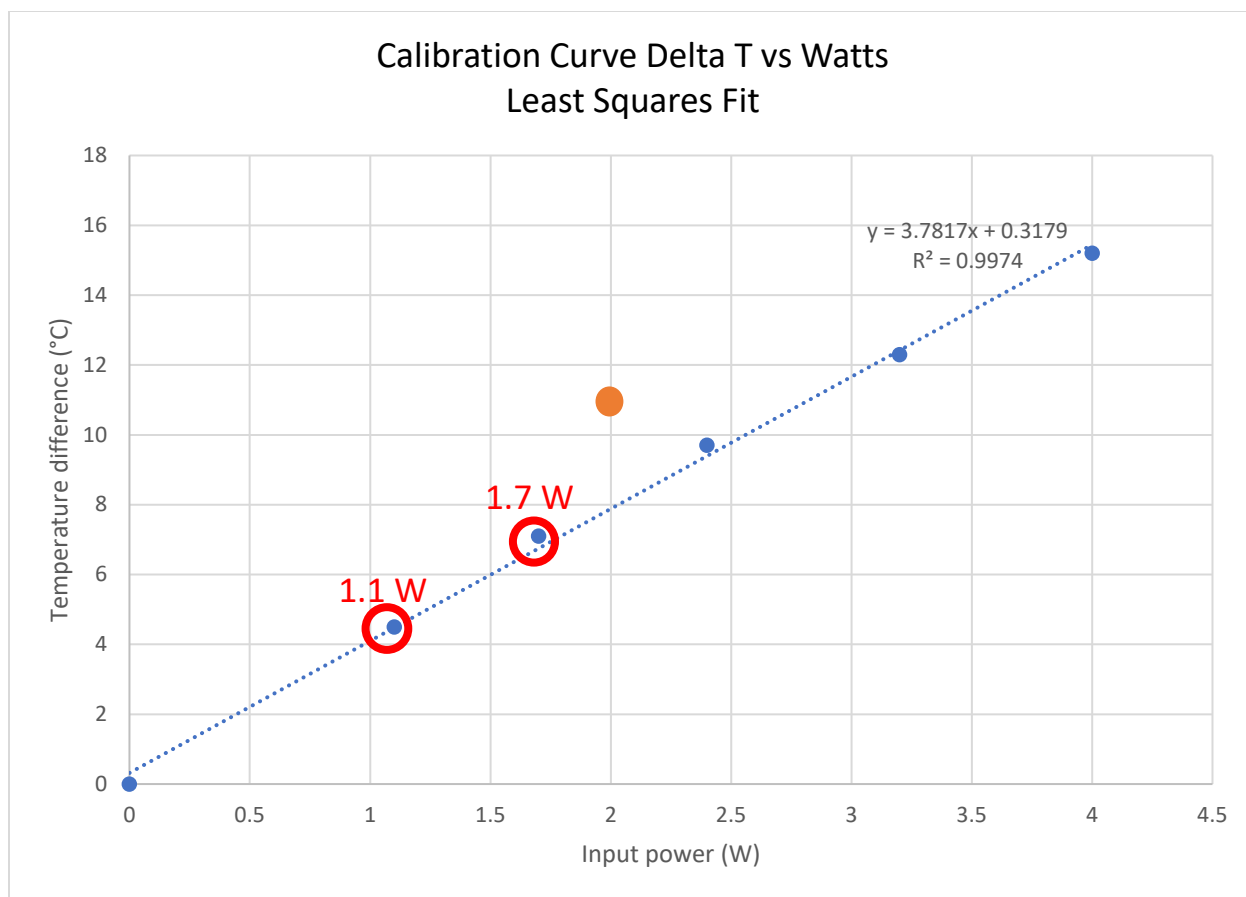
Figure 3. A calibration curve using the two points from Fig. 2, and three higher points from other tests. ● = a hypothetical result above the calibration curve, with 2.0 W input and 2.8 W output; 0.8 W excess heat. The curve must go through the origin (0, 0). Graph courtesy D. Nagel, George Washington U.

Heat losses from a cell should be controlled and consistent within a range of temperatures and power levels. In a properly constructed calorimeter, within a range of ~20°C, the response is linear: for each watt of power, the temperature goes up the same amount. You draw a calibration curve (Figure 3). You derive the heat transfer coefficient (also called the calibration constant), which in this case is 4.0°C per watt, or 0.25 W per degree Celsius. Suppose that during a cold fusion test, you input 2.0 W and the temperature rises 11°C (Figure 3, orange dot). It is above the calibration curve. From the heat transfer coefficient, you determine the cell is producing 2.8 W total (11°C × 0.25 W/°C). That is, 2.0 W of input power plus 0.8 W of excess heat.

Each cell will have a different calibration constant. It depends mainly on how well insulated the cell is. The more the insulation, the more the temperature changes for each watt of input power. The coefficient is measured during calibration at several different power levels, including levels below and above the expected output heat from the experiment.

A well-designed calorimeter will return to the same temperature each time the same power level is input. It should reach that temperature in a reasonable amount of time, perhaps an hour or so. A cell that is too well insulated might take several hours, or even a day, which is unwieldy. Both calibrations and tests will take too long.

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A calorimeter is designed to work within a given range of power levels and temperatures. Above or below that range, it may not work correctly. Figure 4 is a curve from Miles showing what happens when power is below the expected range, which is about 0.6 W with this instrument. At lower power levels heat losses from the lid of the cell begin to dominate, and the curve turns up sharply. [12]

$$P = 0.0376 + 0.1331\,\Delta T$$
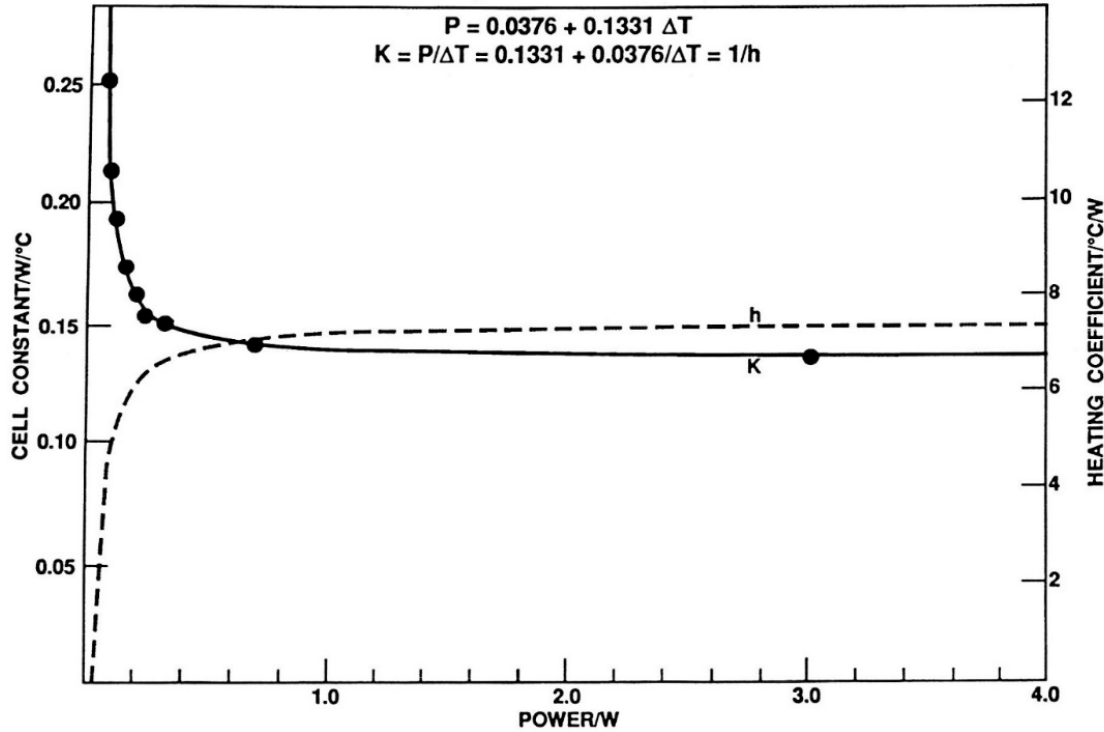$$K = P/\Delta T = 0.1331 + 0.0376/\Delta T = 1/h$$

Figure 4. At low power losses from the lid of the cell begin to dominate, and the response is no longer linear. K: apparent cell constant, h: heat transfer coefficient.

Noise may also be a problem at low power. A calorimeter that can measure to the nearest 0.1 W might not be able to accurately measure the difference between 0.0 and 0.1 W, because noise interferes, whereas it might reliably measure the difference between 1.0 and 1.1 W.

To summarize, here is a rigorous textbook [13] definition of isoperibolic calorimetry by Hemminger and Hohne, with my comments in blue:

The term "isoperibol" operation refers to the use of a calorimeter at constant temperature surroundings with a possibly different temperature of the measuring system. The thermal resistance R_{th} between the measuring system and the surroundings is infinitesimally small in isothermal calorimeters, of finite magnitude in isoperibol calorimeters . . . and infinitely large in adiabatic ones . . . Due to the existence of a finite, defined thermal resistance R_{th} between the measuring system and the surroundings, the heat exchange depends in a definite manner on T_M [temperature of measuring system] and T_F [temperature of the surroundings outside the cell] only . . . Since T_F is constant in an isoperibol operation, the heat flux will be a function of T_M only. This relationship is generally linear; it can be determined by calibration. It is

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noteworthy that the temperature of the measuring system (T_M) changes by heat exchange with the surroundings until an equilibrium is established. This process necessitates a certain interval of time. After a certain time of operation, constant generation of heat in the measuring system (long-lived radioactive sample, for example) brings about a constant temperature T_M. . . .

In other words, with a sample producing a steady, stable amount of power, the temperature of the measuring system rises for a while and then reaches a plateau. During calibration this plateau is one data point.

The isoperibolic method works best with a stable, long-term reaction such as a long-lived radioactive sample.

An adiabatic calorimeter is a well-insulated cell. Heat from the reaction is retained in the cell as much as possible. Heat is measured by multiplying the specific heat of the cell contents by the rise in temperature. The cell soon cools off, so this technique can only be used for quick reactions such as rapid burning of a small sample. These instruments are sometimes called "bomb calorimeters." They cannot be used with cold fusion because the cold fusion reaction sometimes takes days to start, and lasts for weeks.

The flux is "generally linear" as shown in Figure 3, but as described below, it is not linear with Fleischmann and Pons' calorimeter.

. . . For accurate measurements it is not absolutely necessary to keep heat losses as low as possible. What is more important is that these heat losses be repeatably dependent on the temperature difference between measuring system [the cell interior] and surroundings, in this case they can be determined exactly by (electric) calibration. Of course, large heat loss reduces the sensitivity of the calorimeter to a considerable extent.

As I explained: "Heat losses from a cell should be controlled and consistent across a wide range of power levels and temperatures . . ." "Sensitivity" means that a calorimeter that rises 1°C per watt cannot measure heat as precisely as one that rises 5°C per watt.

Electrochemistry, Dewar vessels

Before examining the details of Fleischmann and Pons' isoperibolic calorimetry, we need to introduce some aspects of electrochemistry as they relate to this experiment.

In a cold fusion experiment, heavy water is decomposed (split) by electrolysis. [7] The heavy hydrogen (deuterium) goes to the palladium cathode, and the oxygen goes to the platinum anode. The cathode readily absorbs the deuterium, but platinum does not absorb much oxygen. Most of the deuterium and oxygen gas bubbles up the surface. It looks like the small carbon dioxide bubbles in a soft drink (Figure 5).

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[7] Heavy water is deuterium oxide, D_2O. Hydrogen has one proton only. Deuterium is hydrogen with 1 proton and 1 neutron. Tritium is hydrogen with 2 neutrons. Hydrogen and deuterium are stable; tritium is not. Heavy water is approximately 1 part in 6000 of all water on earth. It is denser than ordinary water, so when you freeze pure heavy water and put the ice cube in a glass of ordinary water, it sinks. Hence the name "heavy water."

The heavy water is mixed with lithium salt to make it conductive. This mixture is called an electrolyte.

Fleischmann and Pons used what is called an open cell, meaning the free deuterium and oxygen leave the cell, going into the open air. This carries off some of the electric input power, while the rest of the electric power heats up the electrolyte. Where total input electrolysis power is V*I (voltage times current) with heavy water electrolysis, the heat in the cell is (V−1.54)*I, where 1.54 is the thermoneutral potential for heavy water. Here is an example from Miles:

Total electric power: 10.12 V × 0.50 A = 5.06 W.

Joule heating in the cell: (10.12 V − 1.54) × 0.50 A = 4.29 W

Heat removed by deuterium and oxygen gas leaving the cell: 0.77 W

In other words, the deuterium and oxygen gas are fuel. If you burned them, you would get 0.77 W of heat. The free deuterium gas molecules drift though the air and eventually recombine with oxygen to form heavy water, releasing the heat.

Because the gas continuously leaves the cell, the electrolyte water level gradually falls. Fleischmann and Pons replenished with make-up heavy water every two days. The lithium salts do not leave the cell, so you only need to add heavy water.

The changing electrolyte level can affect the calorimetry. Fleischmann and Pons developed a simple but clever cell that avoids this problem. The cell is a Dewar vessel. A Dewar is a glass thermos flask (Figure 8), with a vacuum jacket with a silver mirror on the inside of the jacket walls. An ordinary Dewar vessel would be a poor choice for an isoperibolic calorimeter. Most of the heat would leave the cell by conduction out from the lid, instead of radiating from the walls into the bath. This would be an unpredictable, nonlinear heat loss. Fleischmann and Pons used a custom-made cell, with a silvered mirror at the top of the vacuum jacket, and a clear glass "window" at the bottom, as shown in Figure 1. Very little heat radiates from the silvered portion. Most radiates out of the clear glass window. The electrolyte rises and falls within the silvered portion. It does not fall below the window, so the surface area of the cell wall that radiates into the bath does not change.
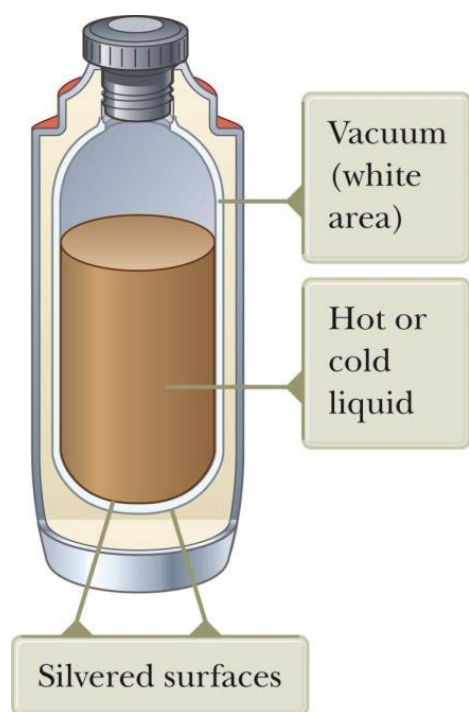

Figure 6. A thermos bottle (Dewar flask), courtesy Hassan Maridi, U. Warsaw.

Complications Ensue

What I described above is a first approximation of the isoperibolic method. A simple conversion factor multiplied by the temperature gives the power (0.25 W/°C in this example). As the textbook says, this is a good method to measure a stable, steady state reaction such as a "long-lived radioactive sample" over a small temperature range.

As I warned, with Fleischmann and Pons, things are more complicated. They measured a dynamic, changing reaction over a wide range of temperatures. They selected a cell that is well insulated, so it produces a large temperature difference. With the NHE experiment, output power ranged from 1 to 5 W (including electrolysis and cold fusion heat). This raised the cell

temperature from ~10 to ~40°C above the bath temperature. The response is not linear. The higher the temperature, the more heat is produced per degree, ranging from 0.095 W/°C at the low end to 0.113 W/°C at the high end. This is because the cell is designed to channel nearly all heat losses through the lower clear window as radiation, and radiation from a surface is proportional to the 4th power of the temperature, the Stefan-Boltzmann law:

Stefan-Boltzmann coefficient × radiant surface area of cell × (Cell temperature in Kelvin^4 − Bath temperature in Kelvin^4)

Because heat increases by the fourth power, a small increase in surface temperature releases proportionally much more heat. Even so, when temperature differences are modest, this does not have much impact, and you can use a simple conversion factor. But when the temperature differences are as large as 40°C you have to use the Stefan-Boltzmann coefficient.

Moreover, things are even more complicated, because with an actual cell you cannot use the textbook coefficient as is. It only works with a perfect vacuum and 100% radiation. Over time, air leaks into the Dewar vacuum, and some of the heat is lost by conduction through the air, instead of radiation. The cell that Miles used at the NHE was about four years old. The vacuum was "soft" (air had leaked in). He calibrated and estimated that the heat transfer coefficient was about 10% higher than it would be with a perfect vacuum. [8]

The Stefan-Boltzmann coefficient tells you the least amount of heat that will be lost from the cell. It is the minimum threshold. If you calibrate and find that even less heat than this is leaving the cell, you have made a mistake. Any real cell will radiate a little more than this, and it will also lose a little heat from other paths, such as conduction along the wires in the lid.

Fleischmann and Pons, Miles and others using this type of cell calibrate to determine the actual heat transfer coefficient. They call this the "pseudo-radiative" coefficient because strictly speaking, it is not entirely radiation.

Working at high temperatures also complicates the calorimetry because it increases evaporation. At low temperatures, evaporation is negligible and can be ignored. But at 50 or 60°C, so much vapor leaves the cell you have to keep track of the enthalpy it removes, or you will underestimate the output. Fleischmann and Pons made careful records of local atmospheric pressure to calculate how much enthalpy was lost by evaporation. They measured how much make-up water was added to the cell and determined that more water was leaving the cell than could be explained by electrolysis. The amount of extra lost water agreed with their estimate of losses by evaporation.

Isoperibolic calorimetry works best with a stable, steady state reaction, but as Miles points out, "there is no steady state in electrochemical calorimetry." Conditions are dynamic, constantly changing. He adds: "major error sources arise from heat flow pathways through the top of the

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[8] The Stefan-Boltzmann coefficient is 5.67×10^{-8} W · m^{-2} · K^{-4}. The cell is 25 cm long with the top 8 cm silvered. The inside diameter is 2.5 cm. The radiation starts at inside surface (diameter 2.5 cm), so the radiative surface is 133.5 cm^2, making the coefficient 7.6×10^{-10} W · K^{-4}. Miles measured the coefficient at 8.5×10^{-10} W · K^{-4}, which is 12% higher.

cell (Figure 4), room temperature changes, fluctuations in the cell voltage due to gas bubble effects, and changes in the liquid levels both within the cell and in the water bath." [12]

On the face of it, you might think Fleischmann and Pons picked the wrong kind of calorimeter. It works best with a narrow range of moderate temperatures, but they wanted to use high temperatures. It works best in steady state conditions, but electrochemistry is never in a steady state. Some critics thought they *did* pick the wrong kind of calorimeter. They should have used a flow calorimeter or some other type that allows a simpler analysis. Fleischmann disagreed, emphasizing that the instrument itself plays a key role in the experiment. It is an integral part of the experiment. You must select the right kind of calorimeter, or the calorimeter itself may interfere or even prevent the reaction. The instrument must allow the sample to get hot. Fleischmann criticized McKubre's isothermal calorimeter because the isothermal technique keeps the sample at a fixed temperature. When the sample produces more heat, the surroundings automatically cool down to compensate.

Why did Fleischmann and Pons insulate their cell so well that it goes to high temperatures with only a few watts of input power? Because high temperatures and dynamic conditions such as rapidly changing current density and temperatures boost the reaction. A cold fusion reaction may occur with the right kind of material when loading and other conditions are met, but when you hold the temperature down close to room temperature, you will probably keep the reaction small and difficult to detect. Fleischmann and Pons emphasized the importance of positive feedback, where a rising temperature promotes the reaction, and the reaction causes the temperature to rise.

They also used high insulation because this increases the sensitivity of the instrument. A small change in power produces a large temperature difference. They could detect reactions even at the milliwatt level. Miles and Fleischmann estimated that with this instrument and the equations they developed, they can measure to the nearest 0.1 mW (0.0001 W). [14]

An Example of a Heat Measurement

Miles ran an experiment at the Japanese NHE laboratory for 69 days in 1997 using an Icarus isoperibolic calorimeter given to the lab by Fleischmann and Pons. Here is an example of excess heat from that experiment: excess heat peaked at 39,100 J on Day 52, which is 0.453 W mean excess power. [9] On day 52, Miles recorded these numbers in his logbook:

T (cell temperature) = 65.15°C = 338.30 K
Tb (bath temperature) = 22.04°C = 295.19 K.
I (amperage) = 0.500 A
E (cell voltage) = 10.12 V
Kr (the cell heat transfer coefficient) = 0.85065E-9 W/K^4

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[9] This is the best result measured with isoperibolic calorimetry during this experiment. On the last day of the experiment, the cell was driven to boiling, producing 118 W excess at peak. That was measured with phase change calorimetry.

The cell temperature was very stable, changing only about 0.080 K/hour. This is good. Stable heat can be measured with more precision than rapidly fluctuating heat.

OUTPUT

Temperature difference (cell minus bath) = 43.11°C

Radiation passed from cell to bath water is $Kr*(T^4-Tb^4)$. Meaning: Heat transfer coefficient × (Cell temperature K^4 − Bath temperature K^4). This equals 4.683 W

INPUT

Total electric power going into the cell is: 10.12 V × 0.5 A = 5.06 W.

Joule heating in the cell is: (10.12 V − 1.54) × 0.5 A = 4.29 W. (Miles computed this to 4 decimal places, 4.2965 W). 0.77 W is carried off as free deuterium and oxygen gas.

EXCESS = OUPUT − INPUT

Excess heat is approximately 4.683 W − 4.297 W = 0.386 W.

That accounts for heat radiated to the bath. Power measured by the calorimeter can be computed with greater precision than this by taking into account other heat loss paths, with the equation in Ref. [14]: [10]

$$P_{calor} = P_{EI} + P_H + P_X - (P_{gas} + P_R + P_C + P_W)$$

P_{calor} = Power balance from all sources. Zero when input and output balance, and the cell temperature is stable. When the cell temperature is increasing slightly, as it was in this case, heat is being stored in it, so P_{calor} is positive.

P_{EI} = Electrolysis Joule heating power. 4.2965 W.

P_H = Internal heater power. (The resistance joule heater is used for calibration. It was not turned on in this instance.)

P_X = Excess power; cold fusion heat, when present. (We want to solve for this.)

P_{gas} = Heat removed by the hot gas as it leaves the cell. This is <u>not</u> chemical potential energy carried off by deuterium and oxygen gas. That is already adjusted for by subtracting the thermoneutral potential (1.54) from the voltage.

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[10] This is a little easier to understand than the "Simplicity" paper equation (described below). Some of these terms are negative. The text says, "As usual, positive quantities represent power added to the system (calorimetric cell) and negative quantities represent power given off to the surroundings." Fleischmann might have made it easier by marking which was negative, but he seldom made things easier for the reader. I have taken the liberty of adding a minus sign for the negative quantities.

P_R = Radiation passed from the cell to the bath water. This is the main energy path. It is where most of the energy leaves the cell. It is 4.683 W in this example.

P_C = Power transferred by conduction (out of the lid, from cell wires and so on).

P_W = Power from pressure-volume work (change in pressure of gas). This is very small; around 0.0023 W

The equation for excess power in Miles' logbook is a little simpler. It does not include P_H because the resistance heater not turned on, or P_C because that is so small. It is:

$$P_X = P_{calor} + P_R - P_{EI} + P_{gas} + P_W$$

That is to say:

Excess power (0.4610 W) = Calorimeter heat balance (0.0100 W) + Radiation passed to bath water (4.6830 W) – Electrochemical Joule heating (4.2965 W) + Power from gas exiting the cell (0.0536 W) + Power from pressure-work (0.0109 W)

Total excess power is 0.461 W, which is a little more than 0.386 W (Radiation to bath only). You add in an extra 0.075 W from the Calorimeter heat balance, Power from gas, and Power from pressure-work. Radiation to the bath is the dominant heat loss path. If there is a significant mistake, it has to be in this term.

Other researchers at the NHE thought that Miles measured the heat transfer coefficient incorrectly. They thought it should be lower, which meant there was no excess heat. This is discussed below in the section "Dispute over when and how to measure the heat transfer coefficient."

Phase change (boil-off) calorimetry in phase 2

Two kinds of phase changes have been used for cold fusion calorimetry: the change from ice to water (melting) and the change from water to steam (vaporization). Dufour et al. [47] reported on an ice calorimeter where the volume of melted ice was measured with a capillary. (The volume decreases as the ice melts. Ice has a larger volume than water, which is why it floats.) In other ice calorimeters, the water from melted ice is measured directly. Fleischmann and Pons, Lonchampt et al. and Lonchampt and Biberian reported on boil-off calorimetry. [4, 15, 16] With boiling phase change calorimetry, heat is measured as the weight of boiled water multiplied by the heat of vaporization: 2259 J/g, or 44 kJ/mol for ordinary water; and 2064 J/g or 41 kJ/mol for heavy water.

After the isoperibolic phase of the experiment described in the "Simplicity" paper, the excess heat is boosted by turning up electrolysis power, to heat up the cathode. This triggers positive feedback. The power can then be turned back down. Fleischmann described this during lectures at ICCF conferences, but I do not think it was clearly stated in their publications. This was a serious omission, in my opinion. They should have made it clear how they triggered the boil-off.

They wrote about positive feedback in general terms, and they wrote a great deal about how heating pulses show the effect is occurring when the temperature does not return to the baseline after a pulse. But I do not recall a paper in which they list the specific power levels, temperatures and duration of the pulses they used to trigger the boil-off events. Biberian and Lonchampt also heated the cell with electrolysis to trigger a boil off. In their case, they did not turn the power up at a chosen time; they let it increase by itself. The cell was operated in constant current mode, usually at 0.5 A. The cell was made of Pyrex, so some silica is leached from it. Various compounds are gradually deposited on the cathode, including silica and lithium. This deposit prevents the passage of current, therefore the voltage goes up. As the voltage increases, the input power goes up, until the temperature reaches boiling. [17]

The boil off method of calorimetry is simple compared the isoperibolic method, hence the title of the paper, "Simplicity."

Once the cell is driven to boiling with positive feedback increasing the cold fusion excess heat, it continues boiling until all of the water is vaporized and the cell is dry.

It takes about 10 minutes for half of the water to boil away. We know it takes that long because they made a time-lapse video of the event with a time stamp on the screen. The time when the boil off was triggered was known. The time when the boil off ends, with all of the water gone from the cell can be clearly seen in the video. Still photos from the video are shown in the paper. The video is on YouTube here:

https://www.youtube.com/watch?v=Tn9K1Hvw434

Unfortunately, this is an old VHS video, and it is a copy of a copy, so the quality is degraded and the picture is blurry, but you can still see when the boil off events begin and end. The video is synchronized with the computer data of temperature and cell electrolysis input power. Fleischmann and Pons explain:

> As it is possible to repeatedly reverse and run forward the video recordings at any stage of operation, it also becomes possible to make reasonably accurate estimates of the cell contents. We have chosen to time the evaporation/boiling of the last half of the D_2O in cells of this type and this allows us to make particularly simple thermal balances for the operation in the region of the boiling point.

Here is the calculation from the "Simplicity" paper [4] with my notes in blue:

CALCULATION

Enthalpy Input
By electrolysis = (E_{cell} − 1.54) × Cell Current ~22,500 J. E_{cell} is the electrochemical term for cell voltage; 1.54 is the thermoneutral potential for heavy water.

Enthalpy Output
To Ambient ≈ k'_R [(374.5°)^4 − (293.15°)^4] × 600 s = 6,700 J. Radiation, based on the Stefan-Boltzmann law that surface radiation is to the fourth power of temperature in Kelvin. In this case, a heat transfer coefficient derived from the surface area and confirmed by calibration, multiplied

by the fourth power of the cell temperature, minus the fourth power of the bath temperature. That is power (W), so it is multiplied here by 600 seconds (10 minutes) to give energy (J).

In Vapour ≈ (2.5 Moles × 41 KJ/Mole) = 102,500 J. That is, 2.5 moles of heavy water (45 g) multiplied by heat of vaporization of heavy water

Enthalpy Balance
Excess Enthalpy ≈ 86,700 J. Excess heat

Rate of Enthalpy Input
By Electrolysis, 22,500 J/600 s = 37.5 W. Electrolysis input power during the boil-off event. This is over-estimated, because the power cuts off when the water level falls below the anode and cathode.

Rate of Enthalpy Output
To Ambient, 6,600 J/600 s = 11 W 11 W power from radiation from the cell to the bath during the event
In Vapour, 102,500 J/600 s ≈ 171 W. 171 W carried off as steam

Balance of Enthalpy Rates
Excess Rate ≈ 144.5 W
Excess Specific Rate ≈ 144.5 W / 0.0392 cm^3 ≈ 3,700 W/cm^{-3}. Power normalized to the volume of palladium

We know this is anomalous cold fusion heat for several reasons:

- As boiling continues, the water level drops below the anode and cathode, so no current can flow between them. Electrolysis stops. But the boiling continues, until all of the water is gone. During a blank test with more electrolysis power, enough to sustain boiling, the moment the water level drops below the anode and cathode and electrolysis stops, and the boiling also stops. Some water remains in the bottom of the cell. It does not boil to dryness.

- The Kel-F plastic support plug holding the anode and cathode in place melts. During the blank test the plastic support remains under water because the boiling stops. It does not melt. Kel-F plastic melts at 300°C, so the cathode must have been even hotter than that, which is why the water continued to boil until it was all gone.

- We know that the heat from the boil off comes from the cathode. Another close-up video of a boiling cell shows that there are no boiling bubbles forming on the anode, only electrolysis bubbles. The two are quite different: bubbles from electrolysis are small and the leave the surface at a steady pace, like the bubbles of carbon dioxide in a soft drink. Bubbles of boiling water are larger and leave more abruptly. (Unfortunately, this video is not available, but that is what it showed.) During a blank

boil-off test with high-powered electrolysis, boiling water forms on both the anode and the cathode.

- We know that nearly all of the water left the cell as vapor. Some skeptics have speculated unboiled water escaped from the cell in foam or spray. If enough unboiled water were to leave the cell, this would considerably lower the enthalpy in vapor. When unboiled water escapes from the cell, it carries the lithium salt with it, so you can estimate how much escaped by measuring the lithium in the cell after the boil-off. Fleischmann and Pons did this, and found only a little lithium was lost, not enough to significantly reduce the heat of vaporization.

This is discussed in two papers, which contradict one another. The first, from 1990, says that some lithium was lost, and this makes it difficult to estimate enthalpy with phase change calorimetry: [3]

It is not possible, however, at this stage to make a quantitative estimate of the heat output [during the boil-off] since the cells and instrumentation are unsuitable for making estimates under these conditions. It should also be noted that, although the cell potential initially decreases (in common to the situation for the bursts) there is usually a change to an increase of the potential with time when cells are driven to the boiling point probably due to the loss of electrolyte in spray leaving the cells.

Biberian also reported that some lithium is lost as spray during boil-off events. [18]

On the other hand, the second report, from 1993, says the amount of lithium lost was negligible. Perhaps they reevaluated the lithium left in the cell by the time this was written: [19]

Douglas Morrison first of all raises the question whether parts of the cell contents may have been expelled as droplets during the later stages of intense heating. This is readily answered by titrating the residual cell contents: based on our earlier work about 95% of the residual lithium deuteroxide is recovered; some is undoubtedly lost in the reaction of this "aggressive" species with the glass components to form residues which cannot be titrated.

Cooling curve analysis in phase 3

After the boil off, the cell sometimes remained hot, for periods ranging from a few hours to a day. Fleischmann and Pons called this phase "heat after death." The "Simplicity" paper describes a heat after death event lasting 3 hours.

There is no input power during this phase. There is no electrolyte, so no current can flow between the anode and cathode. When there is no power going into an object that is warmer than the surroundings, and the object does not produce heat internally by itself, it must cool down. It cools down according to Newton's law of cooling. This curve is monotonic, meaning it always falls, and never rises.

During the heat after death episode described in this paper, the inside of the cell does not cool down according to Newton's law. On the contrary, it remains at the same temperature for a while, and then the temperature rises. We know the palladium cathode is the only thing in the

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cell that produces heat. The amount of heat can be estimated by comparing the cooling curve to a blank test with platinum and heavy water.

Figure 7 shows the cooling curve for a blank test. Cooling begins quickly and then gradually slows down, until the curve is nearly flat at 11,000 seconds (3 hours). Cooling is monotonic.
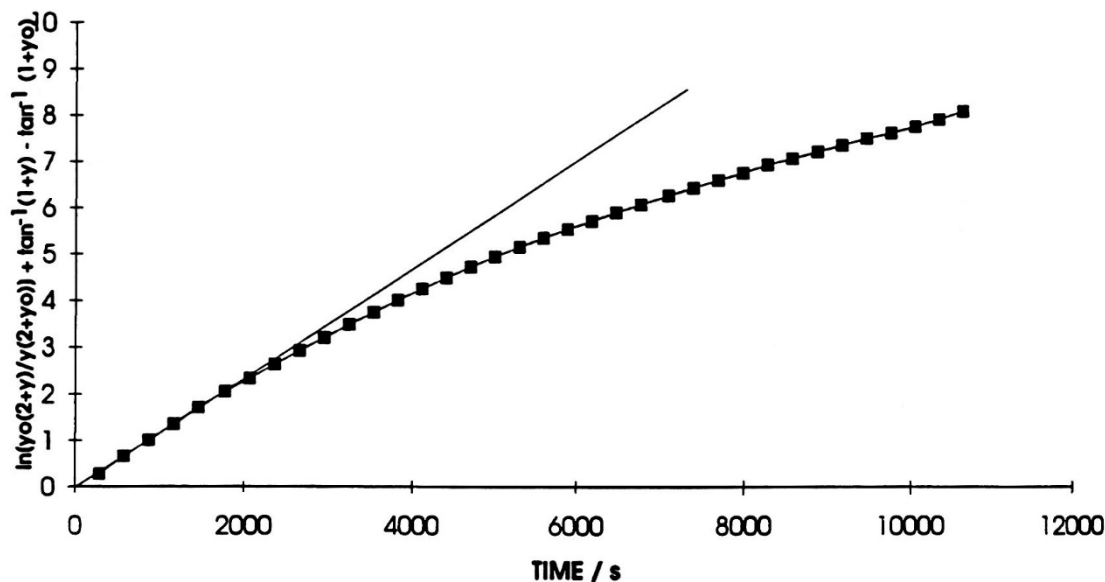

Figure 7. Analysis of the cooling curve for a "blank cell." A rising curve indicates a falling temperature. (Cooling is up, not down.) From Ref. [5]

Figure 8 shows the cooling curve during heat after death. The event lasts much longer; around 32,000 seconds (9 hours). It begins with rapid cooling, but at around 15,000 seconds the cooling levels off, and then at 18,000 seconds it reverses; the cell starts to get warmer instead of cooler. After that, the cell gradually cools, but at a much lower rate than the blank cell, which means it is producing excess heat. At 25,000 seconds there is another reversal; once again, the cell generates more heat than it loses to the surroundings. Finally, at 34,000 seconds it begins to cool at about the same rate as the blank cell, which means the cathode is no longer producing excess heat.
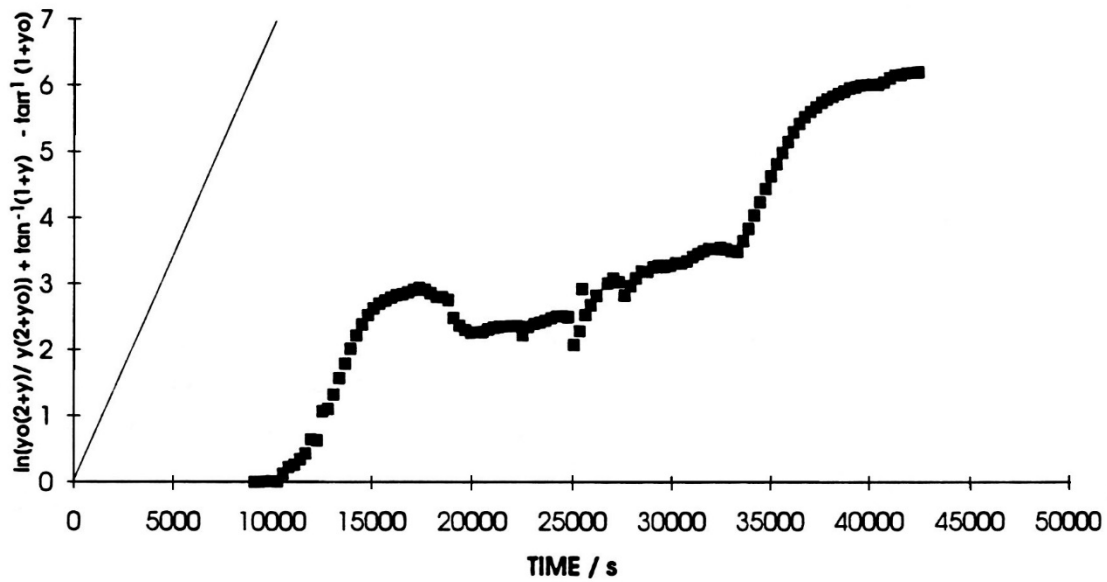
Figure 8. Analysis of the cooling curve with heat after death. Again, a rising curve indicates a falling temperature. (Cooling is up, not down.) From Ref. [5].

Here is the same data converted to excess heat and to the cooling rate. The cooling rate at 18,000 seconds, 22,000 seconds and 25,000 seconds is negative, meaning the cell is heating, not cooling.
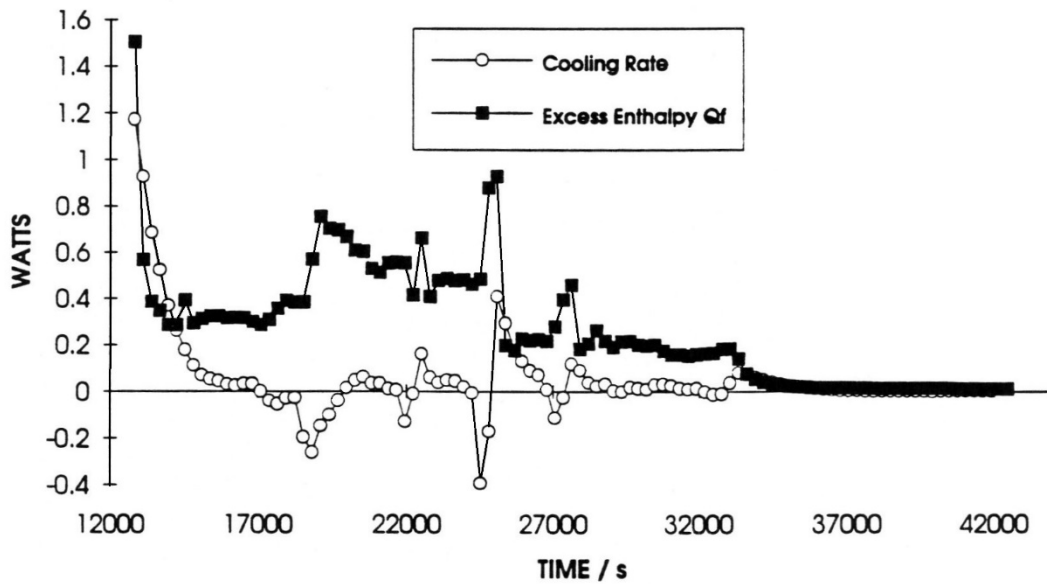

Figure 9. The same data as Figure 6, converted to excess heat and the cooling rate. Cooling is down in this figure, unlike the previous two. From Ref. [5]

Fleischmann and Pons "Simplicity" paper

The paper *Calorimetry of the Pd-D$_2$O system: from simplicity via complications to simplicity.* [4] describes the three methods. At first glance, this paper is not notably simple. The section "Modelling of the Calorimeters" begins with a long equation. It looks forbidding, but it is only the textbook definition of heat from electrolysis, plus one additional term: excess enthalpy. That is, anomalous excess heat produced by cold fusion. To help the reader, the authors included a description of the equation:

Change in the enthalpy content of the calorimeter = enthalpy input due to electrolysis − enthalpy content of the gas stream + excess enthalpy + calibration pulse − time-dependent heat transfer coefficient * (effect of radiation + effect of conduction)

The symbols in this equation are listed in the Glossary of Symbols Used at the end of the paper. The reader might be confused by the K_R notation in this equation and in most other papers by Fleischmann and Pons. It means heat transfer coefficient. It has subscripts such as $[k_R']_{11}$. This is explained in Appendix C of this paper.

In the section below the equation, the individual terms are explained. This is a very detailed analysis. It includes some terms that hardly need to be included because they are so small. For example, there are two terms relating to the changing electrolyte levels in the cell. As electrolysis progresses, water leaves the cell as free deuterium and oxygen gas. The water level falls. Every two days, make-up water is added. These changes in water level affect the calorimetry two ways: they change the heat capacity of the cell, and they change the surface area of the wall that radiates heat. These two effects are covered by two terms in this equation. The first

$$\left[1 - \frac{(1+\beta)It}{2FM^0} \right]$$ "allows for the change of the water equivalent with time." This means that the

heat capacity of all of the water metal and glass of cell is calculated and converted to the equivalent thermal mass for heavy water in moles. When the cell heats, the change in temperature multiplied by the specific heat of heavy water tells us how much energy is being retained by the cell itself. The second term (which is the same except λ replaces β),

$$\left[1 - \frac{(1+\lambda)It}{2FM^0} \right]$$ "allows for the decrease of the radiant surface area with time." As the water falls,

less of the surface area of the cell wall is heated, so less heat radiates from this wall into the bath. Both of these effects are at the milliwatt level. The latter has been almost negated altogether with the silvering at the top of the cell and the clear glass window: ". . . as we have already noted, this term may be neglected for calorimeters silvered in the top portion (however, this term is significant for measurements made in unsilvered Dewars) . . ."

Fleischmann and Pons analyzed their calorimetry from first principles. They analyzed every measurable heat transfer path from the cell to the surroundings. This is so difficult, and so exacting, that many researchers do not even try to do it. They simply calibrate and then use the calibration curve to determine whether there is excess heat, as described above.

Fleischmann and Pons did not only analyze from first principles, they also calibrated extensively and showed that the excess heat was above the calibration curve.

Their pursuit of detail is relentless. So much so, in a sense it may be a disservice to readers. People may get the impression that you must work through many equations describing detailed physics in order to confirm the cold fusion effect. You must take into account the change in water level, which has only a minute effect. The reader might think: "If cold fusion can only be detected by keeping track of such tiny details, it must be very a small effect. Why else would they make made such strenuous efforts to measure it down to the milliwatt. It must be difficult to detect. It might be a mistake. All of this esoteric physics and all these parameters might hide some error."

I wish Fleischmann and Pons had started off by emphasizing that in the first approximation, the excess heat is easy to detect with a simple analysis. They made extremely precise instruments, and they boosted the precision with the complex analysis that took into account many small factors. Their instrument is remarkably simple, yet it was so good, it detected heat at milliwatt levels. They did this not because you must have milliwatt precision to see cold fusion, but because they wanted to look closely. They wanted to examine the reaction in detail, and they wanted to detect it the moment it appeared. They also did this because Fleischmann liked "simple hardware with complicated software," as he put it, where "software" often meant computation done by him, using pencil and paper, including pencil graphs on graph paper. (Fleischmann liked graphs; he said the eye is the best and most important tool for analysis. Ref. [20], p. 14.)

Jean-Paul Biberian thinks that without such a precise instrument, they would not have discovered the effect. He wrote: "Many new discoveries have been made by development of new instruments: microscopes to see microbes, telescopes to see the satellites of Jupiter, there are many examples. In the case of Cold Fusion, it is the creation of a high precision electrochemical calorimeter. Without such a precise and simple instrument they could not have made the discovery." [21]

The papers are crammed with technical details. The discussion of water levels was hammered home with many equations. So were some other details that could hardly have had a measurable effect. There were even discussions of things that could not have happened. For example, they devote considerable attention to hypothetical effects at different atmospheric pressures. In one figure, they show a simulation of how the water might evaporate from the cell if it did not boil. This would take 2.3 hours. The atmospheric pressure would have to be different than the actual recorded pressure that day. They wrote:

The evidence for the time dependence of the cell contents during the last stages of operation is discussed in the next section. Fig 7C shows the values of $\left(k_R'\right)_{11}$ calculated using two assumed atmospheric pressures, 0.953 and 0.97 bars. The first value has been chosen to give a smooth evaporation of the cell contents ($M^0 = 5.0$ D_2O) i.e., no boiling during the period up to the point when the cell becomes dry, 50,735 s. However, this particular mode of operation would have required the cell to have been half-full at a time 2.3 hrs before dryness.

Furthermore, the ambient pressure at that time was 0.966 bars. We believe therefore that such a mode of operation must be excluded.

The fact is, the water <u>did</u> boil. They saw it boil. And the half-time to boil was only 10 minutes, not 2.3 hours. The hypothetical 2.3 hour scenario is so different from the actual situation, it seems contrived to me. It is almost as if they are going out of their way to show how rigorous they are, as if to tell the reader: "see, we thought of everything!"

The analysis and the software associated with this calorimeter are complex, but the cell itself is elegant, simple, and incredibly accurate and precise. It has many advantages, described in Ref. [22]:

- It is inexpensive, so you can afford to make many cells and test them in parallel, as shown the "Simplicity" paper and the video.

- When the cells are placed in a glass enclosed bath, you can see inside the cells through the window at the bottom. This is particularly important during boil-off experiments.

- Radiation as the method of heat transfer has advantages such as "no memory." Gas bubbles or stagnant layers of water forming on the inner cell wall have no effect on the radiative heat transfer coefficient. Thermocouples and small nuclear detection devices can be inserted into the cell without affecting the calorimetry.

- The two main parameters in the calorimetry are 1. the heat transfer coefficient (k_R) which does not change over the course of the experiment; and 2. the total thermal mass of the cell (C_pM). This does change, but it is measured with precision. It is the thermal mass of all cell components including glass, heavy water, electrodes, thermistors, the resistance heater and so on, converted to a single number equivalent to moles of heavy water with that thermal mass. (It is interesting to note that J. P. Joule also converted everything in his cell to the equivalent thermal mass of water. [23])

The other hardware, such as the water bath, is expensive. The thermostat keeps the temperature to within ±0.01°C. [14]

Controversy

In the 1990s, skeptics raised many objections to the work of Fleischmann and Pons. These objections fall into three groups:

1. Emotional and ad hominem attacks, such as claims that cold fusion researchers are lunatics and criminals. There are thousands of these, everywhere from the Washington Post [24] to Wikipedia, but I will not discuss them here. A few samples are in Ref. [25].

2. Many papers asserted that the effect violates theory, so the results cannot be correct. For example, it was said that fusion at these power levels must produce a large flux of

neutrons, powerful enough to kill the observer, yet no such flux occurred, so this cannot be fusion. This is a logical error. It violates the scientific method. When replicated experiments conflict with theory, the experiments are right, and the theory is wrong. Skeptics made many other logical errors. However, these errors are beyond the scope of this paper, which is about calorimetry, so they are relegated to Appendix B of this paper.

3. Assertions that there were errors in the calorimetric instruments and methods. Most of these critiques were in informal venues such as conferences and internet discussion groups. As far as I know, only five peer-reviewed papers have been published that attempted to find errors in calorimetry, by Morrison and Shanahan. [26-30] (See also the rebuttals to Shanahan. [31, 32]) In my opinion, these papers have no merit. Readers are invited to read them and judge for yourselves.

Critics claimed there were errors in detecting neutrons, which was correct. Fleischmann and Pons used a BF3 counter incorrectly. Fleischmann admitted this soon after the first paper was published.

In the five papers cited here, and in countless informal venues, critics claimed there were errors in the calorimetry and the excess heat was not real. For the remainder of this review, I will discuss claims that apply to the three methods of calorimetry in the "Simplicity" paper. I will attempt to show that these claims were mistaken. As far as I know, no one has published a paper that attempts to show an error in the reflux calorimeter published after the "Simplicity" paper.

Before I discuss specific errors, let me point out a general problem with these critiques. As far as I know, other than Shanahan, no skeptic has attempted to show an error in any of the independent replications by researchers such as Storms, McKubre or Miles, or papers from the Italian National Laboratories (ENEA). [33-36] Skeptics have focused exclusively on the early reports by Fleischmann and Pons, as if the rest of the literature does not exist. Indeed, many of them claim the experiment was never replicated, and there *is* no other literature. Skeptics have found no errors in other experiments using isoperibolic calorimetry, although there are dozens of examples. They have found no errors in mass-flow calorimetry, Seebeck calorimetry, boiling and ice phase change calorimetry, or infrared camera detection of excess heat.

Perhaps the skeptics feel that it would be futile to look for errors in all of these experiments, with all of these varied techniques. For good reason –

One of the fundamentals of experimental science is that when an effect is detected with two or more different systems, there cannot be one systematic error. When you detect excess heat with isoperibolic, mass flow and Seebeck calorimeters, that is three different systems, based on three different physical principles. If they are all wrong, there must be three separate systematic errors. Not only do you have to find three different errors; you have to explain why they show the same basic behavior. They all fit the McKubre empirical equation, where the heat increases with loading, current density and flux. [37] You have to show why palladium and heavy water produce an effect, but platinum and heavy water do not. This is an impossible task. It is inconceivable that changes in current density, or the choice of palladium instead of platinum, can

somehow trigger the same kind of errors, to the same extent, in physically different instruments. Even if you postulate that the choice of palladium might influence a <u>thermistor</u> placed in the electrolyte of a cell, it would not also:

influence a <u>thermocouple</u> the same way;

or a set of thermocouples outside the cell, placed against a copper sheath wrapped around the cell;

or thermocouples placed in the flow of cooling water some distance from the cell, in a mass flow calorimeter;

or the thermoelectric devices surrounding the cell at a distance, in a Seebeck calorimeter.

To imagine that all of these devices in these different configurations respond the same way, and *the wrong way*, to the presence of palladium, and they only do this when that palladium is loaded with deuterium to high levels and held at high current densities, is to engage in magical thinking.

Let us turn to assertions that specific, quantifiable errors have been made in the "Simplicity" paper. Such assertions can be debated and falsified.

After Fleischmann and Pons revealed the discovery, many scientists justifiably wondered whether they might have made a mistake. They asked every question they could think of that might reveal a problem. Four main potential problems relating to calorimetry were:

1. Insufficient mixing might produce temperature variations which look like excess heat.
2. A recombination error might be occurring.
3. The cathodes were not hot enough to be fusion. This is not a valid objection. Scientists who say this are confusing power and energy.
4. Dispute over when and how to measure the heat transfer coefficient.

These objections were quickly answered and put to rest, but unfortunately, they continue to be raised to the present day.

Insufficient Mixing Error

The first objection to the calorimetry was the claim that the electrolyte might not be well mixed. If that were true, the temperature might vary from one spot in the electrolyte to another. If the temperature sensor happened to be placed in a warm spot, the researcher might mistakenly conclude that the cell is producing excess heat.

Assume that the electrolyte is warmer some places than others. Assume that a small temperature probe that can only detect the temperature in one limited space in the liquid is placed somewhere in the cell where the liquid happens to be warmer than average. If you compare this temperature to the calibration curve, you might mistakenly conclude there is excess heat.

This is a legitimate concern. However, before they revealed this experiment, Fleischmann and Pons thought carefully about how to do the experiment and how to avoid this error, and many others. They conducted tests and calibrations to be sure the electrolyte was well mixed.

When this objection was raised, they responded to the critics immediately, explaining what they had done, and they later described the steps in detail. They demonstrated that there are no significant variations in the electrolyte temperature because the fluid was well mixed. They used two methods:

They made a video of a drop of red dye dropped into a cell. They used the video to measure the time it took for the dye to be stirred. [3] The bubbles from electrolysis rapidly mixed the dye into the rest of the electrolyte, in less than 3 seconds horizontally, and 20 seconds vertically. This was done at the lowest electrolysis power level they used. The higher the power, the faster mixing occurs. They also addressed this issue by using an array of 5 thermistor temperature sensors (Thermometrics Ultrastable Thermoprobes). The array could be set vertically or horizontally, measuring temperature variations in either direction. They found that variations in the liquid were at most 0.005°C, except at the bottom of the cell, where they were 0.01°C.

I suppose most scientists who read these papers would be convinced that stirring was not a problem. Those who were not convinced could have confirmed these methods by doing electrolysis with ordinary electrodes. They would not need to do cold fusion *per se*. They would not need to use palladium. They could have used steel electrodes in a cell of the same shape and configuration as the cold fusion experiment, at the same power levels, using dye or an array of thermistors. They would have confirmed that the bubbles from electrolysis at these power levels stir the cell enough to eliminate any significant temperature variations.

You can also confirm that the liquid was probably well mixed by reading the papers and thinking about the results. Suppose the liquid was not mixed. Putting the temperature probe in a warm spot would produce false excess heat, but it is equally likely you would put it in a cold spot and see false excess cold. This is impossible. There are no endothermic electrochemical reactions with these materials. You would know that is an instrument error. Furthermore, Fleischmann and Pons would see spurious excess heat or excess cold during "blank" test calibrations with platinum electrodes and heavy water. They did not see any heat in these tests.

It was reasonable to raise these objections at first, but once they were answered, it became unreasonable to continue to raise them, especially when you could verify stirring by doing electrolysis yourself. Yet many people continue to raise these objections. In fact, this "stirring" controversy was one of the reasons the experiment was dismissed early in 1989, even after Fleischmann and Pons showed the video of dye mixing on national television.

Even now this objection continues to be raised. Critics continue to assume there was a mixing problem. [38] They could not have seen the video or listened to what Fleischmann and Pons said. They ridiculed Fleischmann and Pons, and later Robert Huggins for supposedly making this error. One recited a disparaging poem:

"Tens of millions of dollars at
stake, Dear Brother,
Because some scientist put a thermometer
At one place and not another."

Fire from Ice [39], p. 144

Author Gary Taubes took this argument to extremes:

. . . The video showed an effervescent cold fusion cell into which a red dye was poured. Within twenty seconds the dye had been evenly distributed throughout the flask. Fleischmann said this proved that "the argument of ineffective mixing doesn't hold water."

The demonstration was impressive; however, it was bogus. Even if the cold fusion cell had huge temperature gradients — say, fifty degrees hotter on one side than on the other — the red dye would have diffused evenly within a very short time. The temperature gradient in the flasks simply had nothing to do with what could be called the red dye gradient.

Bad Science, p. 271 [40]

This is impossible. How can the temperature be different if the water is mixed? When you pour cold milk into hot coffee and stir, does Taubes think the milk remains cold? Does he think that Maxwells' demon is rushing around inside the coffee, pushing energetic molecules from one side to the other? Furthermore, when there is a measurable temperature difference in water, it is never as large as 50°C. It is a fraction of a degree at most. It is never horizontal, "from one side to the other." A small, vertical temperature difference may be found in liquid that has been sitting for a while, with stagnant thermal gradients. As soon as the liquid is stirred, the gradients go away. Here is what Taubes apparently thinks might happen: You stir a cup of coffee, so that it is completely mixed in a few seconds. You pick it up and take a sip. You find it is hot. You put the cup down, turn it around, pick it up again and take a sip from the other side of the cup. You find it is at room temperature, 50°C cooler.

The ideas offered by Taubes, Shanahan and others not only violate elementary laws of physics, they violate common sense in ways that a five-year-old child would understand.

Taubes is not a professional scientist. His views are not important. But his book is important because it tells us a lot about the scientists opposed to cold fusion. The book impressed many of them, including two Nobel laureates who wrote blurbs for it. They could not have read it carefully, because it is full of mistakes and weird ideas like the 50°C temperature difference.

Moreover, the book is based on interviews with scientists who are listed in an appendix. Nearly all of them are strongly opposed to cold fusion. Taubes says they told him many of the peculiar things in the book, for example, that cold fusion researchers measure voltage but not amperage. On NPR, he said someone told him that cold fusion researchers detect excess heat on weekends because factories are closed and there is more electricity. This is wrong on many levels. There is never "more electricity." Power companies reduce output when demand falls. Power supplies are regulated and do not produce more electricity even if voltage rises. The power is monitored and recorded in an experiment, so if there was excess electricity, it would be recorded. Finally, if this could happen, it would happen during calibration, and it would be noted. The fact that Taubes believes this nonsense is unimportant. The fact that professional scientists told it to him, and Nobel laureates endorsed it, *is* important.

During the first phase of this experiment, with open cell electrolysis, what is called a "recombination error" might occur. It cannot happen during the second and third phases.

As described above, electrolysis decomposes water into hydrogen and oxygen gas, which flows out of an open cell into the atmosphere. Some of the electric power heats up the water. From the example given by Miles above:

Total electric power: 10.12 V × 0.5 A = 5.06 W

Joule heating in the cell: (10.12 V − 1.54) × 0.5 A = 4.29 W

Heat removed by deuterium and oxygen gas leaving the cell: 0.77 W

That is assuming the gas leaves the cell. Suppose it does not. Suppose that instead of leaving the cell, the oxygen gas bubbles swirl around, come in contact with the cathode underwater, and combine with the deuterium to form water. Or, suppose there is a catalytic metal mesh in the headspace above the waterline. The oxygen and deuterium gas bubbles up out of the water, impinges on the metal, and forms water, which falls back into the cell. None of the gas leaves the cell. This is called recombining, and the mesh is called a recombiner. This is how a closed cell works. Without a recombiner, the gas pressure in the headspace in a closed cell will build up until the cell fractures.

Imagine that Miles does not realize the gas is recombining underwater or on a headspace recombiner. He does not realize that none of the gas leaves. He mistakenly thinks there are 0.77 W of anomalous cold fusion heat. [11] This is a recombination error. A result that produces less than total input electric power might be from recombination. How do we know he and the other researchers did not make this error? Because:

1. With this voltage and amperage, recombination cannot produce an error larger than 0.77 W. If you see heat above this limit, you can be sure it is not all coming from recombination. Many experiments in the literature have produced heat above the limits of recombination.

2. If the heat continues after electrolysis is turned off, or after the cell boils dry, it cannot be coming from recombination. Recombination can only happen during electrolysis. In phases 2 and 3 of this experiment electrolysis was off. There are other experiments in the literature in which electrolysis was turned off, but heat continued, for about 4 days in one case. [41]

3. Most definitively, electrochemists measure how much gas leaves the cell. Miles, Fleischmann and Pons and the others confirmed there was no significant recombination in the cell. They did this in various ways. The most common method is to measure the electrolyte water level. It fell the predicted amount every day, showing that the free

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[11] It is a little more realistic to imagine that half the gas recombines underwater, Miles does not notice that, and he thinks there is ~0.39 W of anomalous heat.

hydrogen and oxygen left the cell. When they replenished the cell, they recorded the amount of heavy water added to it. Some of them also measured the gas flow rate with a gas flow meter or with the gas bubbling into an upside-down test tube held underwater.

4. Many other researchers, such as Storms and McKubre, used closed cells, with a catalytic recombiner in the headspace. These cannot have a recombination error. When there is no anomalous heat, the heat release in the cell must equal input electric power.

5. Since a recombination error is impossible in the second and third phase of this experiment, and since it was producing heat in those phases, it was probably producing heat in phase 1 as well. It is unlikely the heat in phase 1 was an instrument artifact, but real heat suddenly turned on in phase 2 and continued in phase 3. It is not possible the heat in all three phases was caused by a single artifact. The methods are completely different. There is no common aspect of the calorimetry that might have gone wrong. To show that all three phases were wrong, there would have to be three different systematic errors that produce roughly the same level of spurious heat. That would be a fantastic coincidence.

The effect might be combustion; the "cigarette lighter effect"

Some critics speculated that Fleischmann and Pons might have observed what the critics called the "cigarette lighter effect." That is, the combustion of deuterium as it degasses from palladium. A few 19th century cigarette lighters were made with palladium loaded with hydrogen.

Kreysa et al. reported that when a palladium sheet cathode loaded with deuterium or hydrogen was placed on a block of wood, the heat from combustion scorched the wood. [42] They said, correctly, that this combustion releases 147.3 kJ per mole D, the textbook heat of formation of water. Kreysa failed to understand the difference between power and energy. Their statements are meaningless. Based on elementary chemistry they should have realized that even though there was enough power to scorch the wood, the cathode produced hundreds of times less energy than Fleischmann and Pons reported even in the first paper, 4 MJ cm^{-3} of electrode volume, over 120 hours.

On cubic centimeter (1 cm^{-3}) of palladium electrode weighs 11.9 grams. On mole of palladium weighs 106 g, so one cubic centimeter is 0.11 moles. Assuming the palladium was fully loaded at a 1:1 ratio with hydrogen, 0.11 moles of palladium holds 0.11 moles of hydrogen or deuterium (0.11 grams) which burns to produce 0.06 moles H_2O. The heat of formation of water is 285,800 Joules per mole, so burning that much hydrogen produces 16,000 J. That is 250 times less than Fleischmann observed. In fact, it is difficult to load as high as 1:1, except at very low temperatures. An actual 1 cm^{-3} sample of palladium loaded by Kreysa's methods would probably produce ~500 times less energy than Fleischmann reported.

Furthermore, in subsequent papers, Fleischmann and others reported much more energy per cubic centimeter.

Kreysa should have understood this. He should have realized the heat he observed only continued for a short time, not 120 hours. He wrote:

We have to report here that as we removed the deuterium loaded palladium sheet from the cell and laid it on the table it scorched the tabletop. One can still argue that this was due to deuterium fusion. Therefore we loaded the palladium sheet cathodically with hydrogen using an electrolyte containing only normal water (no enriched heavy water) and laid it on a piece of wood, where it also burned a scald (see Fig. 2). This demonstrates qualitatively that hydrogen released from hydrogen loaded palladium can be oxidised catalytically to water if oxygen is present. This catalytic recombination reaction

$$2 D_2 + O_2 \rightarrow D_2O \; H_R° = -147.3 \text{ kJ/mol D}$$

was not considered by Fleischmann and Pons.

Fleischmann and Pons are electrochemists, so of course they considered this. Kreysa is an electrochemist, so he should have known this produces hundreds of times less energy than they reported, even though it momentarily produces enough power to scorch wood. Any high school student should know the difference between power and energy.

Kreysa surely knows that nuclear reactions often produce less power than a chemical reaction from the same amount of material, but more energy. As described above, the Curies measured 0.012 W from a 0.1 g sample of radium. The power density is far too low to scorch wood. A wooden kitchen match weighs 0.2 g. It produces about 40 W of heat, 3,300 times more than the radium, and of course it will scorch wood. It burns out in 25 seconds, after producing about 1,000 J of energy. The radium remains warm, producing 378,000 J per year. The half-life is 1600 years, so a thousand years from now it will still be producing 245,000 J per year.

Other scientists made this same mistake, such as George Chapline (Lawrence Livermore National Laboratory), who said: "It is possible that Fleischmann and Pons have rediscovered a 150-year-old German cigarette lighter." (May 1989). (Ref. [39], p. 102)

Douglas Morrison repeatedly cited the "cigarette lighter effect," long after people pointed out to him that he was confusing power and energy. He published a long discussion of the "cigarette lighter effect" in a peer reviewed paper in 1994, citing Kreysa. Morrison claimed the effect might explain the boil off and heat after death reaction described by Fleischmann et al. in the "Simplicity" paper. [2][19]

. . . the "cigarette lighter effect" has been forgotten. . . . In the simple calculation used for stage three [heat after death], a significant effect is omitted, of the heat produced by the catalytized recombination of the hydrogen with the oxygen. The oxygen is released from the anode by electrolysis, and towards the end when the cell is about dry, from the air. There is no mention in Fleischmann and Pons's paper of any attempt to measure the amount of oxygen, deuterium and water in the gases and vapours leaving the test tube.

Before Morrison published, Fleischmann sent him a rebuttal:

In the first place we note that the explanation of Kreysa et al. could not possibly have applied to the experiment in question: the vapourisation of the D_2O alone would have required ~1.1MJ of energy whereas the combustion of all the D in the palladium would at most have produced ~650J (assuming that the D/Pd ratio had reached ~1 in the cathode), a discrepancy of a factor of ~1700. In the second place, the timescale of the explanation is impossible: the diffusional relaxation time is ~ 29 days whereas the phenomenon took at most ~6 hours . . . Thirdly, Kreysa et al confused the notion of power (Watts) with that of energy (Joules) which is again an error which has been promulgated by critics seeking "Chemical Explanations" of "Cold Fusion". . . .

Fleischmann also pointed out that at the fastest rate hydrogen diffuses, it would take hours to emerge and it would only produce 5 mW in combustion heat, whereas this effect produced 145 W. Morrison saw Fleischmann's response, and he rewrote parts of his paper to account for it, but he went ahead and published the "cigarette lighter effect" portion.

How did Kreysa, Morrison and others make this error? Morrison was a professional scientist at CERN, one of the world's top laboratories. He must have understood advanced physics to do his job. The difference between power and energy is middle-school physics. It seems extremely unlikely that he did not understand this, or that Kreysa did not, but I cannot rule that out. People have gaps in their education, and blind spots. Still, this is like not knowing the difference between current and voltage. It is a mind-boggling error.

I am sure Morrison did not make a careless error which he forgot to double-check. Morrison saw Fleischmann's response. Comparing different drafts of Morrison's critique, and the dates they were circulated, we see that Morrison corrected some of the other problems Fleischmann pointed out, but not this one. Either Morrison did not understand the difference between power and energy, or he acted in bad faith hoping to convince the readers there was a problem where he knew there could not be one.

Taubes' motivation was clear. He told Edmund Storms he did not care whether cold fusion is real or not; he was writing the book to make money.

Insufficient data points

Steven Jones, Morrison, and other critics complained that the timescale of the data in the *Simplicity* paper was insufficient. Data points were taken 5 minutes apart, which they said was not often enough. There may be spikes and power excursions in between the data points. This objection was first raised by Morrison at the ICCF3 conference. In response, Fleischmann showed an oscilloscope trace of the power, which is at much higher resolution. There were no spikes.

This issue can also be addressed two other ways. First, many data points were taken over the weeks leading up to the boil off, both when there was no excess heat and later after excess heat began. If there were spikes and excursions, they would show up in some of these data points even though the points are 5 minutes apart, because over 16 days there are 4,600 data points. That is enough to show spikes, assuming spikes happen at random intervals. Second, after the boil off has been in progress for some time, the water level falls below the anode and cathode, so

no power can flow through the cell. Yet the boiling continues. There can be no input power during this phase, so there can be no spikes or excursions.

Dispute over when and how to measure the heat transfer coefficient

When Miles did a 69-day experiment at the NHE laboratory, based on the heat transfer coefficient that he and Fleischmann computed, he concluded the experiment produced excess heat. Other researchers at the NHE computed a lower heat transfer coefficient and concluded there was no excess heat.

In 1989, Lewis et al. at the California Institute of Technology did an experiment and concluded it did not produce excess heat. They began with one heat transfer coefficient, and they repeatedly increased it, by 14% in all, so that the results always came out to zero. Fleischmann, Miles, Noninski and others pointed out that it was more likely the coefficient remained the same and there was 14% excess heat.

In both cases, researchers disagreed about how to measure the coefficient, and when during the course of the experiment it should be measured. These two cases are discussed below.

Fleischmann and Pons begin by measuring the heat transfer coefficient in blank tests with a platinum cathode in heavy water. Heavy water has a slightly different thermal mass and thermoneutral potential than ordinary water, so this is a little more accurate than a blank test with ordinary water.

Soon after they begin a test with palladium in heavy water, they measure the heat transfer coefficient again. This is called calibrating on the fly. They usually do this with a heat pulse (described in Ref. [20], pages 14-18). If, after the pulse, the temperature falls back to the same level it was at before the pulse, they assume the pulse reveals the change in cell temperature per watt. This works even if there is excess heat, as long as the heat is steady; the pulse is on top of the excess heat.

Many researchers calibrate on the fly by measuring the temperature per watt of input power soon after the experiment begins. This technique works because a bulk palladium electrochemical cold fusion experiment seldom produces heat in the first few days. So, there is no excess power and the temperature rise is only caused by the input power, the same as with a platinum cathode in a blank test. This may not work with a thin-film experiment, which sometimes loads quickly and soon starts producing heat. The palladium-boron cathode used by Miles at the NHE also produces heat quickly, sometimes the first day. This complicates things.

Take the example shown in Figure 3, with the coefficient of 4.0°C/W. Suppose you do not know the coefficient. You want to measure it on the fly after the experiment begins. You assume there is no excess heat, and you measure a temperature difference of 11°C with 2 W input (the orange dot). You think the heat transfer coefficient is 11°C/2 W = 5.5°C/W. To avoid this mistake, you need to look for the lower bound heat transfer coefficient for the entire experiment, not just one time. Suppose you measure:

Day 1: 11.0°C, 2 W input, 5.5°C/W coefficient
Day 2: 13.0°C, 3 W input, 4.3°C/W coefficient
Day 3: 4.2°C, 1 W input, 4.2°C/W coefficient

The lower bound is 4.2°C/W. You assume this is the coefficient when there is no excess heat. You go back to Day 1 and apply this: 2 W × 4.2°C/W = 8.4°C; 11°C − 8.4°C = 2.6°C, which translates to 0.6 W excess. Actually, you are a little off. You underestimated the excess, because you did not realize that in the last measurement, there was 0.05 W of excess heat, and without that the temperature would be 4.0°C, not 4.2°C.

The lower bound coefficient sets the zero for the entire experiment. You accidentally shifted the zero line up 0.05 W. This method is safe because you can never overestimate heat, even though you might underestimate it. The method works well with Fleischmann and Pons' calorimeter because most heat transfer is by radiation, so you know the value cannot be lower than a pure Stefan-Boltzmann coefficient. If it is, something is wrong with the instruments or data analysis.

This method does not work when you assume there is no excess heat and you measure the coefficient only once. That is what the researchers at the NHE did. They measured the temperature difference on Day 3 of the experiment; they assumed there was no excess heat that day. They derived a lower bound coefficient smaller than the one Miles and Fleischmann did. It turned out there *was* heat on Day 3. They also forgot to take into account 0.25 W from the resistance heater; they underestimated the thermal mass of the cell; and they made some other errors described in detail by Fleischmann. [9]

A graph of the data shows that something is amiss with the NHE coefficient.

Miles measured the coefficient every 5 minutes over the entire experiment, and found that the lowest number was on Day 61, which is the data point shown in the red circle in Figure 10. He computed the lower bound heat coefficient for that day at 0.85065E-9 W/K^4 and he applied that to all data points. Figure 11 shows the same data graphed with the NHE coefficient, 0.793504E-9 W/K^4. This result is impossible. It shows the cell producing excess heat some days, and a heat deficit on other days (an endothermic reaction). The net result of these positive and negative excursions is approximately zero: no net excess heat was produced. Because an endothermic reaction is impossible under these conditions, the NHE researchers concluded that either there was something wrong with the calorimeter, or something was wrong with the methodology recommended by Fleischmann. They concluded that Miles did not observe excess heat.
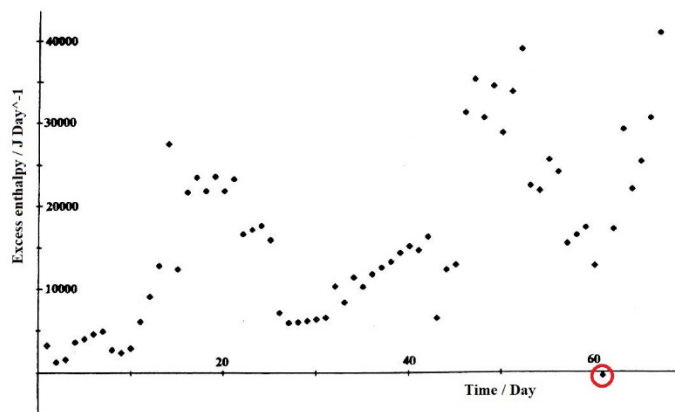
Figure 10. Excess enthalpies in the NHE experiment computed using the lower bound heat coefficient based on the ICARUS Methodology instructions by Fleischmann, which he gave to the NHE. The data point at Day 61 (red circle) is at the zero line, with no excess heat.
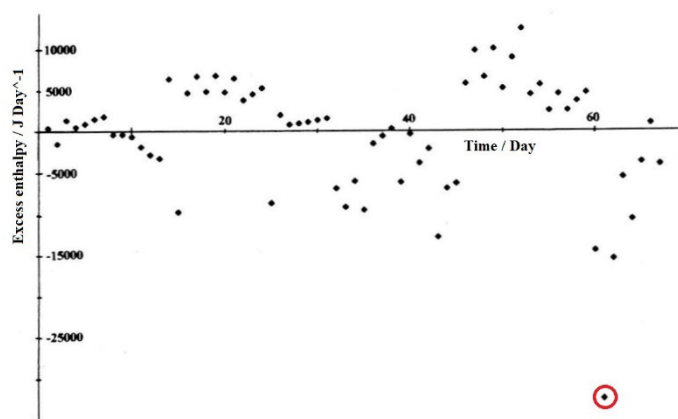

Figure 11. Excess enthalpies using NHE procedure. The data point at Day 61 (red circle) shows negative 30,000 J, which is impossible. The NHE coefficient has shifted the zero 30,000 J too high.

Early in the history of cold fusion, Lewis at the California Institute of Technology made a similar mistake. [43] He kept raising the zero line. He saw a higher temperature with the same input power, gradually increasing by 14%, but instead of assuming that it was caused by excess heat, he assumed that the heat transfer coefficient was changing. He thought that at the beginning of the test, 1 W caused the temperature to rise 14.0°C, but later it caused the temperature to rise 15.9°C. Lewis described the changes in coefficient:

> We . . . sometimes observed abrupt or gradual changes in the rate of heat loss from these cells, presumably resulting from a change in the rate and/or form of gas evolution. These changes often resulted in a sustained temperature rise of the cell (which might be interpreted in terms of the onset of excess enthalpy production), but recalibration with the load-resistor method during this period showed no evidence for any anomalous power production, even after the reported activation period for the Pd rods had been exceeded.

Lewis presumed the change was caused by a change in gas evolution, but he did not confirm this by measuring the gas flow, or by measuring the loss of electrolyte. In his recalibration test

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for excess heat, he assumed that cold fusion heat is exactly proportional to current density, and it responds to changes in current density immediately. To look for excess heat, he reduced electrolysis input power (and thus current density) and added in the same level of resistance heating power to compensate. Total power going into the cell was the same. He looked for reduced anomalous heat in response to the lower current density. He did not see it. The temperature did not fall. But his assumption was wrong: cold fusion heat does not always respond in exact proportion to current density. It does not respond immediately, either. In some cases, it continues for hours after the power is turned off, in heat after death. Lewis' method of checking will not reveal any change if cold fusion heat continues at the same level even after current density is reduced.

Miles described this is technical terms: [12]

The experimental observation by N. Lewis that $P'_{EL} + P'_{Re} \approx P_{EL}$ simply cannot prove that there is no excess power but only that $P_X - P'_X \cong 0$, i.e., the change in P_X is small when a portion of the electrolysis power is replaced by resistor power. It is interesting to note from Table 2 that the input power ($P'_{EL} + P'_{Re}$) required to maintain a constant cell temperature in the Lewis study is always smaller for the experiment at the higher current density. This effect is consistent with the presence of an anomalous excess power that increases with the current density and is near the magnitude reported by Fleischmann et. al.

And: [22]

The most disturbing aspect of the Caltech report concerns the heating coefficient in a Pd/D$_2$O+0.1 M LiOD experiment that was allowed to increase with time from 14.0 KW^{-1} (0.0714 WK^{-1}) at 14.7 hours to 15.9 (0.0629 WK^{-1}) KW^{-1} at 115.0 hours. This could just as well have been interpreted as a 13.6% excess power effect. Experiments at Caltech for Pd/H$_2$O + 0.1 M LiOH gave lower heating coefficients ($h = 12.5 \pm 0.7$ KW^{-1}) that did not show this large increase with time. Using a constant h value of 14.0 KW^{-1} yields excess power that increases with the electrolysis time up to 76 mW. The excess power density of 1.0 W/cm^3 Pd for an analysis of the Lewis study is in excellent agreement with reported excess power in other F-P experiments using similar current densities.

I summarized it more simply: [44]

Lewis may have observed the same level of excess heat that Fleischmann and others did with similar materials and electrochemical conditions. But instead of concluding that he was seeing 14% excess heat, Lewis concluded that the instrument had changed 14%. He did not specify a reason why it might have changed, and he did not perform recalibration tests that would confirm the change and pinpoint the source of the error in the instruments.

Mallove described it best:

Don't stand on the scale when you zero it out.

Fleischmann, Miles and others pointed out these problems to Lindley, the editor at *Nature*, in letters to the editor. Noninski and Noninski found other problems as well. Lindley says that he sent the critique to Lewis himself for "advice." In other words, he asked Lewis whether a critique

of his own paper should be accepted or rejected, and Lewis decided that his own work was fine. This is not how peer-review is supposed to work.

Readers are invited to [read comments by Lewis, Lindley, Fleischmann and the others](), and decide for yourselves who is right.

Acknowledgements

Appendix A. Could 18th and 19th century calorimeters have measured the cold fusion effect?

Martin Fleischmann once remarked that their method of calorimetry was developed by J. P. Joule in the 1840s. Joule measured the heat from electric resistance heaters to discover Joule's law (heat = current^2 × resistance). He later measured the heat from electrolysis, which is what Fleischmann and Pons did. [23]

This comment prompted me to wonder whether Joule could have detected cold fusion with his instruments. I decided to do a test with a cell similar to his (Figure 12). Joule had difficulty with ambient temperature changes. I deliberately left the windows and doors of the house open in spring weather, so that ambient temperatures would be uncontrolled.
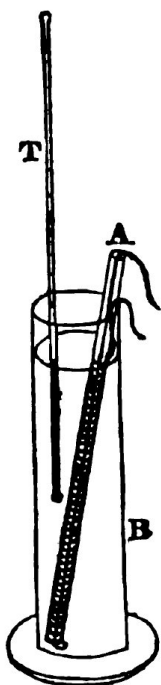

Figure 12. The cell used by J. P. Joule to establish Joule's law. A: coil of wire (resistance heater); B: glass jar partly filled with water; T: thermometer.

I used a thermistor with 0.1°C precision, and an analog voltmeter and ammeter. The power supply could be set to 5 levels from 1.1 to 4.0 W. I set it to each level several times, measured the ambient and cell temperatures, and then computed the average temperature difference between the cell and ambient air (Table 1). Figure 2 (above) shows calibrations at 1.1 and 1.7 W, and Figure 3 shows the calibration curve.

Table 1. Average temperature differences with a rudimentary calorimeter

Input power (W)	Temperature difference (°C)	Degree/Watt	Watt/Degree
1.1	4.4	4.091	0.244
1.7	7.1	4.177	0.239
2.4	9.7	4.042	0.247
3.2	12.3	3.844	0.260
4.0	15.2	3.800	0.251
	Average:	3.991	0.251

Joule described uncontrolled ambient air temperature changes: the "difficulty which exists in keeping the air of the room in the same state of quiet, of hygrometry, &c. during the different days on which the experiments were made." Joule's thermometer was about twice as sensitive as mine, with 0.1°F increments. Joule used adiabatic rather than isoperibolic calorimetry. In other respects, his experiment did resemble Fleischmann and Pons'.

I concluded that even with my crude instrument, or with Joule's 1841 instrument, many cold fusion reactions could have been detected with confidence. I am sure these instruments can measure 1 W with confidence, and probably ~0.5 W. Storms looked at 124 notably successful experiments, and counted 84 above 1 W, and 20 more above 0.5 W. [45]

Needless to say, Fleischmann and Pons' calorimeter was far more accurate and precise than Joule's instrument, or the crude instrument I devised. I deliberately let the ambient temperature change by as much as 2°C. They controlled the bath temperature to within ±0.01°C. They used high stability thermistors, with 0.02% stability per year, calibrated against NIST thermometers. So, they could reliably measure at the milliwatt level. Their analysis was incomparably more accurate and complex than my first approximation. It was based on first principles, whereas I use a junior high school textbook approximation.

I did this test partly to refute skeptics who claim this effect is very difficult to detect. I showed that any competent scientist in the last 150 years could have detected many cold fusion reactions. Actually, many reactions might have been measured with the first modern calorimeter, made by Lavoisier and Laplace in 1780. This was an ice calorimeter. [13] They used it to measure the metabolism of a guinea pig, to confirm metabolic heat and carbon dioxide are in the same ratio as they are from combustion. The heat from the guinea pig melted 447 g of water over 10 hours, which is a heat release of 149,097 J. Divided by 10 hours that is 3.91 W. This is close to the modern estimate of guinea pig metabolism, 2.67 W.[12] [46] They measured the water to the nearest 4 g (1 drachme). Thus, the smallest heat release they could measure was 4 g × 333.55 J/g = ~1,334 J. If there had been only 4 g of melted water in 10 hours, I suppose it would have evaporated, making it difficult to measure accurately. I suppose they could measure 4 g in 1 hour (3,600 seconds) without much difficulty, which means they could measure 1,334 J / 3,600

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[12] The guinea pig was inside an ice calorimeter, so it might have generated more body heat than usual because it was cold. However, it was in a nest, and Lavoisier and Laplace reassure us, "the animal did not seem to have suffered in these experiments."

seconds, or power to the nearest 0.37 W, which is impressive. This would be good enough to confirm cold fusion heat above 1 W.

The researchers at Shell Oil made an instrument similar to Lavoisier's ice calorimeter, albeit more sensitive. They measured the heat from a cold fusion reaction with it. [47]

Appendix B. Unscientific objections to cold fusion

Many unscientific objections to cold fusion have been raised. The most common is that it violates theory because it does not produce radiation the way plasma fusion does. Therefore, it cannot be fusion, so it must be an experimental error. This turns the scientific method upside down. The fundamental rule of science is that experiments are the only standard of truth. Experiments define the phenomenon. They show that cold fusion cannot be chemical, because the cell has no chemical fuel and it produces thousands of times more heat than any chemical reaction. It produces helium in the same ratio to the heat as plasma fusion, which makes it fusion by definition. It does not produce radiation, so it cannot be the same mode of reaction as plasma fusion.

Granted, experiments must be widely replicated at high signal-to-noise ratios before you can rely on them. A one-off report of cold fusion should not be believed. But these experiments have been replicated hundreds of times in over 180 laboratories. [45] If these experiments conflict with the laws of physics, that can only mean the laws are incorrect.

Whether the experiments actually conflict with theory is an open question. Some theorists said they do, while others such as Julian Schwinger and Peter Hagelstein said they do not. Either way, theory can never be the basis to reject a replicated experiment.

John Huizenga, the head of the DoE ERAB panel that dismissed cold fusion in 1989, concluded his book with a 6-point summation. [48, 49] Point 5 is that no violation of nuclear theory is possible no matter what the experiments show, and therefore point 6 is that since the effect cannot be nuclear and it cannot be chemical, we know *a priori* that all positive cold fusion excess heat results must be errors:

5. If the reported intensity of nuclear products is orders of magnitude less than the claimed excess heat, then the excess heat is not due to a nuclear reaction process.

6. Furthermore, if the claimed excess heat exceeds that possible by other conventional processes (chemical, mechanical, etc.), one must conclude that an error has been made in measuring excess heat.

Huizenga felt no obligation to show a technical error in the experiments. They had to be wrong, based on his interpretation of nuclear theory. Beaudette summarized points 5 and 6: [50]

In sentence 5, he implicitly denies the possible existence of unknown processes by allowing it no place in the logic of his presentation. For those readers who do not notice the missing element, his statements lead to a pervasive confusion about the field.

The final sentence 6 is coupled tightly to sentence 5. Five denies the availability of conventional fusion sources, and six denies the availability of non-nuclear energy sources. Voilà, there is no such thing as anomalous power.

What sentences 5 and 6 assert is that nuclear measurements are science, and calorimetric measurements are not science. Throw away their measurements and keep mine. I wonder if there can be found in science a more narrow, a more provincial view of one's professional specialty than is held in these sentences.

There have been many other confused notions about the scientific method, such as the idea that an experiment cannot be accepted until anyone can easily replicate it. On the contrary, many experiments can only be replicated by experts with a great deal of difficulty. For example, the next set of tokamak plasma fusion experiments will require thousands of experts working at the ITER reactor, a multibillion-dollar installation. No other facility in the world will be able to perform these experiments. No one claims that plasma fusion does not exist because it is so difficult to replicate. A related idea is that an experiment cannot be accepted unless the replication is nearly always successful. If that standard had been applied, no one would have believed transistors were real in the early 1950s when many of them failed; or that rockets were real in the late 1950s when most of them exploded; or that cloned animals are real when only one in a thousand survived to birth. The failure rate for finding the top quark would be astronomically high if you count the 20 billion proton-antiproton collisions it takes to produce one top quark.

Critics have made many other logical errors, especially in the 2004 DoE review. Rothwell and Melich made a list of 14 of the most egregious errors. [51]

Appendix C. [kR′] Heat Transfer Coefficient Format

Fleischmann and Pons used the designation [k_R'] where R is the radiative heat transfer coefficient, with 2 or 3 subscripts: [k_R'] $_{i, j, l}$. The subscripts mean:

i Method of analysis. 1=Differential; 2=Backward integration; 3=Forward integration

j When present: Time period of measurement cycle. When there are only two subscripts this term is not included.

      j=5, times somewhat above the origin
      j=6, times somewhat above t_1 [application of calibration pulse]
      j=7, times somewhat above t_2 [cessation of calibration pulse]
      j=8, combination of times for j=6 and j=7

l Indicates 1=Lower bound; 2=True

Thus:

$[k_R']_{11}$ indicates: Differential, Lower bound.

$[k_R']_{262}$ indicates: Backward integration; Time period 6; True value.

A single bar over the k_R' term indicates this is an 11-point average value, where values are measured every 5 minutes (55 minutes):

$$\overline{k_R'}$$

The double bar, used in other documents, indicates a double average; that is, 6 of the 11-point averages combined ($6 \times 55 = 330$ minutes total):

$$\overline{\overline{k_R'}}$$

Source: Miles, M., M. Fleischmann, and M.A. Imam, *Calorimetric Analysis of a Heavy Water Electrolysis Experiment Using a Pd-B Alloy Cathode* 2001, Washington: Naval Research Laboratory, pages 4-5. Averages described on page 12.

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