



ELSEVIER

28 February 1994

PHYSICS LETTERS A

Physics Letters A 185 (1994) 498–502

Comments on claims of excess enthalpy by Fleischmann and Pons using simple cells made to boil

Douglas R.O. Morrison

CERN, Geneva, Switzerland

Received 10 June 1993; revised manuscript received 5 October 1993; accepted for publication 14 December 1993

Communicated by J.P. Vigiér

Abstract

Fleischmann and Pons have claimed to have performed a “simple” experiment and to have observed excess enthalpies larger than 1 kW/cm^3 of palladium. It is shown that in fact the system they use is exceedingly complicated, is under-instrumented and that they have ignored several important factors so that it is unclear whether or not they have observed any excess heat.

1. Introduction

M. Fleischmann of Southampton and S. Pons of IMRA Europe, have published in *Physics Letters A* [1], a communication entitled “Calorimetry of the Pd–D₂O system: from simplicity via complications to simplicity”. There they claim evidence for the production of specific excess enthalpy larger than 1 kW/cm^3 of palladium in a Pd–D₂O system. They comment that this is comparable with the rates obtained in a fast breeder reactor. They note that the reproducibility is high. In this Letter serious doubts are expressed about the justification of this claim and the methods used to derive it – the experiment is not a simple one but is exceedingly complex. Thus this Letter will only consider the major claims of more than 1 kW/cm^3 (stages 3, 4 and 5 below).

Essentially they perform electrolysis in small tubes which are open so that the gases and vapour can escape freely. The cathodes are rods of palladium of 0.2 cm diameter and 1.25 cm length giving a total volume of 0.039 cm^3 . Note that a specific excess enthalpy of 1 kW/cm^3 , would correspond to only 39 W

for the very small volume of palladium actually used. A thermistor was placed above the level of the top of the palladium rod – this gave the only temperature measurement inside the tube.

The two cells with D₂O in 0.1 M LiOD solution, mentioned in Fig. 8, are considered. There are five stages.

2. Stage 1

For 3 and 9 days, the cells receive a current of 0.2 A and are calibrated/refilled 1 and 7 times, respectively.

It was noted that at short times (hours in Fig. 9a) the heat transfer coefficient is markedly negative, that is, there is negative excess enthalpy – this they ascribe to the heat of absorption of deuterium ions entering the lattice.

3. Stage 2

The current is increased to 0.5 A and the temperature jumped to over 50°C. This stage lasts 16 days

minus 14 hours. The cells are calibrated/refilled once per day, this is about 15 times. During this time, as shown in Fig. 8, the voltage rises at first slowly and then more and more steeply and the temperature similarly rises slowly and then steeply, until the cells are at about 85°C (as indicated in Fig. 11). This stage ends about 14 hours before the cells boil dry (Fig. 11).

4. Stage 3

This lasted about 14 hours. It was the time until the cells boiled dry minus the final 600 seconds.

From Fig. 11, the temperature of one of the cells (which had 3 days at 0.2 A) goes from 86°C to 100°C. There is no clear sign of any calibration/refilling during this time. From Fig. 10b, the specific excess enthalpy derived varies erratically between about 15 and 30 W/cm³ – since the volume of the palladium is 0.039 cm³, this means the actual excess enthalpy claimed is only about 0.6 to 1.2 W. The calculation is made using a complicated non-linear regression analysis of the system which includes a square heating pulse (from the resistive heater in the cell) and adding D₂O to replace loss of liquid due to evaporation and electrolysis as indicated in Figs. 4 and 5 – this heat pulse and its effects are the basis of the calibration.

5. Stage 4

The last 600 seconds before the cell is dry.

The behaviour near and during boiling is observed using a video camera. From this video, the time for the cell to go from about half-empty to dry, is taken – more precisely the amount of liquid boiled off is estimated over the final 10 minutes before the test tube was declared dry. A new and apparently simple calculation is made in which the enthalpy input is taken as

$$(\text{cell voltage} - 1.54 \text{ V}) \times (\text{cell current})$$

and the enthalpy output is assumed to be composed of two terms, the energy radiated and the heat resulting from the vaporization of the D₂O remaining in the cell 600 seconds before it is dry (this latter term

is dominant). It is this simple calculation that gives the highest values claimed, namely “the excess rate of energy production is about four times that of the enthalpy input” and that the specific excess enthalpy is 3.7 kW/cm³ of palladium.

6. Stage 5

The authors note some further important features. “Following boiling to dryness and the open-circuiting of the cells, the cells nevertheless remain at high temperature for prolonged periods of time (Fig. 11); furthermore the Kel-F supports of the electrodes at the base of the cells melt so that the local temperature must exceed 300°C”. No explanation is given and Fig. 10 is marked “cell remains hot, excess heat unknown”. From Fig. 11 it may be seen that the temperature recorded on the thermistor above the palladium stays just above 100°C for 3 hours and then falls sharply.

7. Calculations of stage 3 – there are two serious problems

Firstly, a complicated non-linear regression analysis is employed to justify the claim of excess enthalpy to be made (this appears to be the “complication” referred to in the paper title). This type of analysis by Fleischmann and Pons [2] has been carefully studied by Wilson et al. [3] who state that “they significantly overestimate the excess heat ... an additional significant overestimate of excess energy occurs when the calibration is made above 60°C”. Now stage two is mainly above 50°C and rising to about 86°C. Further Wilson et al. write “Because of the paucity of experimental details in their publications, it has been difficult to determine quantitatively the effect of calibration errors”. A reply by Pons and Fleischmann [4] did not address [5] the main questions posed by Wilson et al. From Fig. 11, it appears that there were no calibrations in the temperature region of stage 3 – this must be considered a major omission in the design of the experiment. It is concluded that it is not possible to say whether or not there is excess enthalpy production.

Secondly, it may be noted in Fig. 8 of Ref. [1], that

the cell voltage rises as the temperature rises and that as 100°C is approached, the voltage rises more and more steeply. Experience by the GE group [5] was that in operating similar open cells over many days, they also noticed a rise in cell voltage with time. They found that this effect was due to some of the escaping gases carrying some lithium salt with them (some dried lithium salts were found outside). As the level of the electrolyte is maintained by adding fresh D₂O (but not any lithium salt), the concentration of lithium in the electrolyte decreases with time and the voltage rises. The GE group confirmed this experimental observation by atomic absorption analysis. The cell resistance rises (causing higher voltage due to the constant current mode operation) due to loss of lithium salts which was caused by entrainment of electrolyte droplets up the gas outlet tube. This may be considered confirmation that even at moderate temperatures, the outlet stream contains liquids as well as gases as will be discussed for stage 4 when the temperature was still higher and the boiling much more vigorous.

It may be concluded that claims of excess enthalpy in stage 3, have not been established.

8. Calculation of stage 4

This calculation assumes that after a liquid level has been visually estimated from the video, ALL the liquid below this level is converted into gas. However this neglects two factors. First, the fluid ejected from the open cell is assumed to be 100% gaseous. But with vigorously boiling, it normally happens that part of the fluid is in liquid form. This entrained liquid should not then be included in the calculation. This possibility is not considered by Fleischmann and Pons and no reports of any measurement of the gas/liquid content of the fluids leaving the test tube is described. Second, a further neglect is that as the liquid is boiling vigorously, it must contain gas bubbles and hence the estimate of the amount of liquid below the estimated level, should contain a correction for gas in the liquid – but also this possibility is not discussed in the Fleischmann and Pons paper. This problem might have been answered if the enthalpy of the fluid escaping from the cell had been measured,

but no indication is given of any such check having been made.

Another important problem is the estimate of the input energy – here the input enthalpy is taken as the current multiplied by the cell voltage – 1.54 V. It is not explained how these quantities are measured. This is crucial as when the cell is boiling vigorously the impedance must be fluctuating strongly. Thus the current will have both an ac and a dc component. If only the dc component were measured, then the input enthalpy would be underestimated. A detailed description of the current and voltage measuring systems showing their fast response characters is needed, but is not presented nor is an adequate reference given to it, so that although the estimate might be correct, there is an absence of proof. Also the cell voltage over the last 600 seconds cannot be read from Fig. 8 as the bin size is 500 000 seconds and the trace is rising exceedingly steeply – as this is an important question, one would have expected the voltage trace over the last 600 seconds to have been shown in great detail.

A further complication has been noted which invokes the “Leidenfrost” effect which is important in fast reactors (which are mentioned in the paper). For these reactors, there are no moderating atoms and the heat transfer rates are such that one cannot cool them by using normal water at 1 atm. This is because of the Leidenfrost effect where the velocity of the water vapour escaping is so great that it stops water from reaching the metal surface. It is like the effect observed when a drop of water falls on a very hot stove.

During the boiling in the last 600 seconds, the possibility needs to be considered of some hot spots on the palladium surface (because it is heated by the electrical current but not cooled by contact with liquid and also if the bubble stayed on the surface long enough, some catalysis could occur heating the spot further). This hot spot would then keep away more liquid because of the vapour layer – so it would get still hotter. The extra turbulence would help to expel the liquid from the small test tube as liquid and not gas. All this is very complex and needs complicated calculations.

The mechanism of bubble formation in bubble chambers was first explained by Frederick Seitz [6]. The important point is that to grow, a bubble needs to be greater than a certain critical radius of about one micron. Below this radius the pressure of the sur-

face tension which is inversely proportional to the radius, is very large and hence quickly kills bubbles whose radius is smaller than the critical radius. The critical radius is reached in a very short time, about a microsecond. Now the palladium surface tends to be pitted after days of electrolysis and would offer a good starting point for nucleation of the bubble. The bubbles would tend to start again and again in the same favoured place. So it could happen that such a locality becomes quite hot which would generate more of the “Leidenfrost” effect. Initially the gas on the surface of the rod would be deuterium, but once the bubble exceeds the critical size, the electrolyte could also supply the gas and this could contain oxygen and hence permit catalyzed recombination. Another question is what does all this do to the impedance? Better information on this is needed.

The whole effect is very complex and made even more complex than in a fast reactor because the metal, palladium, acts also as a catalyst to recombine the oxygen and deuterium in the gases present! And this would help to heat the hot spot still more. And there is also an electric current passing.

Again whether or not there has been any excess enthalpy, cannot be decided from the paper as important considerations are not discussed, information is missing, and there is no indication of or reference to proper measurements and controls that should have been performed.

9. Effects of stage 5

The melting of the Kel-F support below the palladium indicating a temperature of above 300°C, is presented as an “important feature”. However there is the “cigarette lighter effect”. In the last century, it was difficult to make reliable matches to light cigarettes. A reliable smokeless lighter was invented which consisted of a rod of palladium into which hydrogen had been introduced under pressure. This caused the lattice of the palladium to expand and thus stored energy. To light a cigarette, the top of the rod was uncovered; some hydrogen escaped releasing some of the stress and thus releasing energy which resulted in a small rise in temperature of the end of the rod. Palladium is a catalyst of hydrogen and oxygen which burn to give water plus energy. The palladium now

slightly heated, catalyzes the escaping hydrogen and the oxygen of the air and the resulting heat of combustion which is mainly deposited on the surface of the rod, raises its temperature. This temperature rise releases more hydrogen which is catalyzed by the still more efficient hot palladium, and so on until the tip of the rod is so hot that the cigarette can be lit. The reliability of this system is high. An interesting recent confirmation of this using electrochemistry was reported by Kreysa, Marx and Plieth [7]. With a hydrogen-loaded sheet of palladium, they “measured, after an incubation time of 15 s, a temperature rise of the palladium from 20°C to 418°C within 74 s”.

The dramatic effect of the melting of the Kel-F support cannot be explained by Fleischmann and Pons as being due to electrolysis since there is no liquid, no current and no electrolysis. However, it is exactly what would be expected with the “cigarette lighter effect” where the hot palladium rod continues to catalyze the interaction of the hydrogen which is slowly escaping from the rod, with oxygen in the cell or from the air.

It might be expected that this effect would occur also with normal water, H₂O, being used instead of heavy water, D₂O, but no report is given in the paper of any results of tests of stages 3 or 4 using normal water, H₂O.

Because the volume of the palladium is so small, 0.039 cm³, the heat given out by the burning of the deuterium inside it, is too small to account for the maintenance of the cell at near 100°C for 3 hours – another explanation is needed. It has been pointed out by Droege [8] that this is a major problem for Fleischmann and Pons to explain why the thermistor records temperatures of remarkable stability, staying within a few degrees of 100°C although before boiling dry there is the input electrical energy of 37.5 W plus their large claimed excess enthalpy of 144.5 W. But after boiling dry and the short-circuiting of the cell, there is still the enthalpy output to ambient (that is radiative heat loss) which they calculate to be 11 W. So how can the temperature be constant (or very slightly rising) for 3 hours when there is 11 W loss, no electrolysis and no incoming energy?

10. Conclusions

The experiment and some of the calculations have been described as “simple”. This is incorrect – the process involving chaotic motion, is complex and many calibrations and corrections are needed. The calculations have been made to appear simple by incorrectly ignoring important factors. It would have been better to describe the experiments as “inadequately instrumented and designed” for the complex nature of the experiment attempted, rather than “simple”. A true “simple” experiment is one where corrections and calibrations can be reduced to a minimum. If one were to insist on using an open cell, then arguments about how much recombination of D_2 and O_2 gases occurs, can be avoided by the standard electrochemistry technique of using a divided cell or an H-cell where the anode and cathode are in the arms of the H so that they are far apart. However, simplicity in calorimetry is best achieved by using a closed cell with a catalytic recombiner (e.g. a heated piece of palladium) and by enclosing the cell in a series (e.g. three) baths which are each kept at constant temperature. The cell is kept at a higher temperature than the innermost bath so that if any excess enthalpy is produced inside, the heating of this bath can be reduced to keep a constant temperature, and the excess is measured simply. Since this is a null measurement system, the necessary calibrations and calculations are simple and straightforward instead of being complicated and ignoring relevant effects.

It is interesting to note that the Fleischmann and Pons paper compares their claimed power production with that from nuclear reactions in a nuclear reactor and this is in line with their first paper [9] where d–d fusion reactions were given and production of neutrons and tritium claimed. It may be noted that

the present paper does not mention fusion nor indeed consider a possible nuclear source for the excess heat claimed.

A number of effects have been presented which have not been considered by the authors before they claimed large excess enthalpies. It is not said here that these effects necessarily explain everything with conventional (that is well-established) science. Until these effects are properly studied by the authors with a well-designed and well-analysed experiment with adequate instrumentation (not just a thermistor and a video camera), and until for all five stages of the experiment, a full description is given of what occurs when deuterium is replaced by hydrogen, it is unjustified to claim any new energy source.

Acknowledgement

It is a pleasure to acknowledge the help and comments of many friends.

References

- [1] M. Fleischmann and S. Pons, *Phys. Lett. A* 176 (1993) 118.
- [2] M. Fleischmann, S. Pons, M.W. Anderson, L.J. Li and M. Hawkins, *J. Electroanal. Chem.* 287 (1990) 293.
- [3] R.H. Wilson, J.W. Bray, P.G. Kosky, H.B. Vakil and F.G. Will, *J. Electroanal. Chem.* 332 (1992) 1.
- [4] M. Fleischmann and S. Pons, *J. Electroanal. Chem.* 332 (1992) 33.
- [5] General Electric group of Ref. [3], private communication.
- [6] F. Seitz, *Phys. Fluids* 1 (1960) 1.
- [7] G. Kreysa, G. Marx and W. Plieth, *J. Electroanal. Chem.* 268 (1989) 659.
- [8] T. Droege, private communication.
- [9] M. Fleischmann and S. Pons, *J. Electroanal. Chem.* 261 (1989) 301, 263 (1989) 187 (E).