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Reply to the critique by Morrison entitled: "Comments on claims of excess enthalpy by Fleischmann and Pons using simple cells made to boil"

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Abstract

We reply here to the critique by Morrison [Phys. Lett. A 185 (1994) 498] of our paper [Phys. Lett. A 176 (1993) 118]. Apart from this general classification of our experiments into stages 1–5, we find that his comments are either irrelevant or inaccurate or both.

In Ref. [1] Morrison presents a critique of our paper [2]. In the introduction to his critique, Morrison has divided the time-scale of the experiments we reported into five stages. In this reply, we will divide our comments into the same five parts:

Stage 1: the cells were polarised at 0.2 A and were calibrated and refilled 1 and 7 times respectively;

Stage 2: the cell current was increased to 0.5 A;

Stage 3: the final stage of polarisation following the last refilling of the cells minus the final ~ 600 s;

Stage 4: the last ~ 600 s during which about half of the D_2O in the cells was boiled to dryness;

Stage 5: a final period lasting about 3 hours during which the cells remain at high temperature.

The principal points in Morrison's critique are (Ia)–(VIa):

(Ia) that we used a complicated non-linear regression analysis to justify the claims of excess enthalpy generation;

(IIa) that according to a critique by Wilson et al. [3] this method of data analysis overestimates the rates of excess enthalpy generation;

(IIIa) that liquid droplets may be expelled from the cell;

(IVa) that there may have been an additional enthalpy input to the cell due to ac components of the cell voltage;

(Va) that there may have been a departure from nucleate boiling;

(VIa) that some of the effects observed may be explained by an additional enthalpy input due to a proposed catalytic recombination of deuterium and oxygen [4].

We make the following observations (Ib)–(VIb) about these points of criticism.

(Ib) *Stages* 1, 2 *and* 3. We did not use this method of data analysis for the results reported in Ref. [2]. We note that Morrison has not drawn attention to the all important "blank experiments" illustrated in Figs. 4 and 6 of Ref. [2] by the example of a Pt cathode polarised in the identical 0.1M LiOD electrolyte. He has therefore failed to realise that a precise calibration of the cells (relative standard deviation 0.17% for the example illustrated) can be obtained in a sim-

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ple way (point-by-point enthalpy balances) using only the assumption that there is zero excess enthalpy generation in these "blank cells". This gives what we have termed the "lower bound heat transfer coefficient, $(k'_R)_{11}$". We have also shown that the precision of $(k'_R)_{11}$ is within 1σ of the accuracy of the true value of the heat transfer coefficient, $(k'_R)_2$, obtained by a simple independent calibration using a resistive Joule heater (see (IIb) below). The application of more complex methods of data analysis [5,6] (beyond the scope of Ref. [2]) shows that the precision of $(k'_R)_{11}$ is also close to the accuracy of $(k'_R)_2$ (this is the complication referred to in the title of our paper [2]). It follows that the calibration of the cells using such simple means can be expected to give calorimetric data having an accuracy set by this relative standard deviation in the subsequent application of these cells.

We draw attention to the fact that the time-dependence of $(k'_R)_{11}$ (the simplest possible way of characterising the cells) when applied to measurements for Pd-cathodes polarised in D_2O solutions, gives direct evidence for the generation of excess enthalpy in these systems. It is unnecessary to use complicated methods of data analysis to demonstrate this fact semiquantitatively; it is even unnecessary to calibrate the cells with a resistive heater.

We note also that Morrison has misinterpreted the behaviour at short times during stage 1. $(k'_R)_{11}$ is initially markedly negative because of the presence of a source of excess heat, see Fig. 9a of Ref. [2]. However, the rate of excess enthalpy generation in this time region is positive, see Fig. 10a of Ref. [2] (not negative as stated by Morrison) and it is this rate of excess enthalpy generation which we have attributed to the heat of absorption of H or D in the cathode.

(IIb) This statement made by Morrison is both incorrect and invalid. It is invalid because we have not used this method of data analysis for the results in this paper; it is incorrect because Wilson et al. [3] did not in any way prove that the application of non-linear regression fitting overestimates the rate of excess enthalpy production. In order to appreciate this point it is unfortunately necessary to comment (see Ref. [7]) on the errors in the critique of Wilson et al. [3].

First, we would like to point out that we have no dispute regarding the particular method of data analysis favoured by the group at General Electric: their analysis is in fact based on the heat transfer coefficient $(k'_R)_2$. If there was an area of dispute, then this was due solely to the fact that Wilson et al. introduced a subtraction of an energy term which had already been allowed for in our own data analysis, i.e. they made a "double subtraction error". By doing this they derived heat transfer coefficients which showed that the cells were operating endothermically, i.e. as refrigerators! Needless to say, such a situation contravenes the second law of thermodynamics as the entropy changes have already been taken into account by using the thermoneutral potential of the cells.

It is important to appreciate that Morrison has misinterpreted the critique of Wilson et al. [3]. Referring to the particular method of non-linear regression analysis Morrison states:

"This type of analysis by Fleischmann and Pons [2] (Ref. [7] in this text) 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'. [1, p. 499]". This statement confuses three quite distinct issues:

firstly, Wilson et al. [3] pointed out that calibrations made above 60°C have to take into account the change in the enthalpy of evaporation of the H_2O or D_2O due to the calibration pulse. We accepted this criticism [7]; indeed, in our work since 1989 (see Ref. [8]), we have always allowed for this effect, e.g. see Eqs. (5) and (6) of Ref. [2]. It follows that this particular criticism does not apply to Ref. [2];

secondly, Wilson et al. [3] did not carry out an analysis of the non-linear regression technique; instead they simply stated that because the results of our analysis did not agree with their own (itself based on a "double subtraction error", see above), the non-linear regression method had to be incorrect;

thirdly, that we used non-liner regression fitting to derive the results in Ref. [2]; we did not do so.

We will leave others to judge whether our reply [7] to the critique by the group at General Electric [3] did or did not "address the main questions posed by Wilson et al." (in the words of Morrison). However, as we have noted above the critique produced by Wilson et al. [3] is in any event irrelevant to the evaluations presented in our paper [2]: we have used the self-same method advocated by that group to derive the values of the excess enthalpy. It is inappropriate that Morrison accepts this method but apparently does not accept the validity of the derived values.

(IIIb) *Stages* 1–5. Morrison raises the question whether parts of the cell contents may have been expelled as droplets especially 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. Furthermore, we have found that the total amounts of D_2O added to the cells (in some cases over periods of several months) correspond precisely to the amounts predicted to be evolved by (a) evaporation of D_2O at the instantaneous atmospheric pressures and (b) by electrolysis of D_2O to form D_2 and O_2 at the appropriate currents; this balance is maintained even at temperatures in excess of 90°C [8].

We note here that other research groups (see e.g. Ref. [3]) have reported that some Li can be detected outside the cell using atomic absorption spectroscopy. This analytical technique is so sensitive that it will undoubtedly detect the expulsion of small quantities of electrolyte in the vapour stream. We also draw attention to the fact that D_2O bought from many suppliers contains surfactants. These are added to facilitate the filling of NMR sample tubes and are difficult (probably impossible) to remove by normal methods of purification. There will undoubtedly be excessive foaming (and expulsion of foam from the cells) if D_2O from such sources is used. We recommend the routine screening of the sources of D_2O and of the cell contents using NMR techniques. The primary reason for such routine screening is to check on the H_2O content of the electrolytes.

(IVb) *Stages* 1–4. The question of the influence of putative ac components of the current is an issue which has been referred to before and which we have previously answered [5]. If one considers the primary physics of power dissipation from a constant current source controlled by negative feedback, then it will be seen that this criticism is not relevant. Our methodology is exactly the same as that which we have described previously [5]; it should be noted in addition that we have always taken special steps to prevent oscillations in the galvanostats. As the cell voltages are measured using fast sample-and-hold systems, the product $(E_{\text{cell}}-E_{\text{thermoneutral,bath}})I$ will give the mean enthalpy input to the cells: the absence of random fluctuations is readily confirmed by direct measurement; the ac component is determined by the ripple content of the current which is $\sim 0.04\%$ of the dc current.

(Vb) *Stage* 4. In this point Morrison establishes the transition from nucleate to film boiling based on his experience of the use of bubble chambers. This transition is a well-understood phenomenon in the field of heat transfer engineering. A careful reading of our paper [2] will show that we have addressed this question and that we have pointed out that the transition from nucleate to film boiling can be extended to 1–10 kW cm^{-2} in the presence of electrolytic gas evolution.

(VIb) *Stages* 1–5. Morrison again introduces the possible influence of the catalytic recombination of oxygen and deuterium as a possible explanation for the observation of excess enthalpy generation notwithstanding the fact that this has repeatedly been shown to be negligible. Thus, as far as the contents of Ref. [2] are concerned, the close agreement of $(k'_R)_{11}$ and $(k'_R)_2$ shows that there is no such source of excess enthalpy during stages 1–3. The schedule of additions of H_2O or D_2O as the case may be and the volumes of the gases evolved (e.g. see Refs. [5,8]) show that the Faradaic efficiencies of the cell reactions are close to 100% during stages 1–4.

We note also that the influences of electrocatalytic reactions can be excluded on quite general grounds. Thus D_2 (or H_2) cannot be reoxidised at the oxide coated Pt-anodes. The maximum conceivable total rate of heat generation based on the diffusion of O_2 through the solution (~ 5 mW for the electrode dimensions used) will be reduced because intense D_2 (or H_2) evolution (and D_2O evaporation during stage 4) degasses the oxygen from the solution in the vicinity of the cathodes. We note furthermore that the maximum localised effect will be observed when the density of putative "hot spots" will be $1/\delta^2$ where δ is the thickness of the boundary layer. This gives us a maximum localised rate of heating of ~ 6 nW. The effects of such localised hot spots will be negligible because the flow of heat in the metal (and the solution) is governed by Laplace's equation (here Fourier's law). The spherical symmetry of the field ensures that temperature perturbations are eliminated (compare the elimination of the electrical contact resistance of two plates touching at a small number of points).

In this context Morrison also asserts that no evidence has been presented in the paper about stages 3 and 4 but using H_2O in place of D_2O. As we have already noted he has failed to comment on our extensive discussion of a "blank experiment". Admittedly, the evidence was restricted to stages 1 and 2 of his own classification, but a reference to an independent review of some of our work [9] will show him and interested readers that such cells stay in thermal balance to at least 90°C.

However, Morrison raises the issue of catalytic recombination principally in order to seek a chemical explanation of stage 5 of the experiments. His description of this stage of the experiments starts with an incomplete quotation of a single sentence in our paper. The full sentence reads:

"*We also draw attention to some further important features: provided satisfactory electrode materials are used, the reproducibility of the experiments is high*; following the boiling to dryness and the open-circuiting of the cells, the cells nevertheless remain at a 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."

Morrison omits the most important part of the sentence, italicised here, including the words "satisfactory electrode materials" which point to the nub of the problem. In common with the experience of other research groups, we have had numerous experiments in which we have observed zero excess enthalpy generation. The major cause appears to be the cracking of the electrodes, a phenomenon which we will discuss elsewhere.

With respect to his own quotation Morrison goes on to say:

"No explanation is given and Fig. 10 is marked 'cell remains hot, excess heat unknown' ". The reason why we refrained from speculation about the phenomena at this stage of the work is precisely because explanations are just that: speculations. Much further work is required before the effects referred to can be explained in a quantitative fashion. In the lengthy section Effects of stage 5 Morrison attempts to interpret our observations in terms of "the cigarette lighter effect". This phenomenon (the combustion of hydrogen stored in palladium when this is exposed to the atmosphere) was first proposed by Kreysa et al. [4] to explain one of our early observations: the vapourisation of a large quantity of D_2O ($\sim$500 ml) by a 1 cm^3 palladium cathode followed by the melting of the cathode and parts of the cell components and destruction of a section of the fume cupboard housing the experiment [10]. Morrison (in common with other critics of "cold fusion") is in favour of such "chemical explanations" of the "cold fusion" phenomena. As this particular explanation has been raised, we examine it here.

In the first place we note that the explanation of Kreysa et al. [4] could not possibly have applied to the experiment in question: the vapourisation of the D_2O alone would have required –1.1 MJ of energy whereas the combustion of all the D in the palladium would at most have produced $\sim$8.4 kJ (assuming that the D/Pd ratio had reached $\sim$1 in the cathode), a discrepancy of a factor of $\sim$130. In the second place, the timescale of the explanation is impossible: the diffusional relaxation time is $\sim$29 days whereas the phenomenon took at most $\sim$6 hours (we have based this diffusional relaxation time on the value of the diffusion coefficient in the α-phase). Thirdly, Kreysa et al. [4] confused the notion of power (watts) with that of energy (joules) which is an error which has been promulgated by critics seeking "chemical explanations" of "cold fusion". Thus Morrison reiterates the notion of heat flow, no doubt in order to seek an explanation of the high levels of excess enthalpy during stage 4 of the experiments. We observe that at a heat flow of 144.5 W (corresponding to the rate of excess enthalpy generation in the experiment discussed in our paper [2] the total combustion of all the D in the cathode would be completed in $\sim$4.5 s, not the 600 s of the duration of this stage. Needless to say, the D in the lattice could not reach the surface in that time (the diffusional relaxation time is $\sim 10^5$ s) while the rate of diffusion of oxygen through the boundary layer could lead at most to a rate of generation of excess enthalpy of $\sim$5 mW.

Having set up this scenario Morrison finds in the last paragraph of this section, that this cannot explain stage 5 of the experiment. In the normal course of events this should have led him: (i) to enquire of us whether the particular experiment is typical of such cells; (ii) to revise his own scenario. Instead, he implies that our experiment is incorrect, a view which he apparently shares with Droege [11]. However, an experimental observation is just that: an experimental observation. The fact that cells containing palladium and palladium alloy cathodes polarised in D_2O solutions stay at high temperatures after they have been driven to such extremes of excess enthalpy generation *does not present us* with any difficulties. It is certainly possible to choose conditions which also lead to "boiling to dryness" of "blank cells' but such cells cool down immediately after such "boiling to dryness". If there are any difficulties in our observations, then these are surely in the province of those seeking explanations in terms of "chemical effects" for "cold fusion". We have observed that the heat transfer coefficient for cells filled with gas (N_2) stay close to those for cells filled with 0.1 M LiOD (this is not surprising because the main thermal impedance is across the vacuum gap of the Dewar-type cells). The "dry cell" must therefore have generated ~120 kJ during the period at which it remained at high temperature (or $\sim 3\ \mathrm{MJ\ cm^{-3}}$ or $26\ \mathrm{MJ\ (mol\ Pd)^{-1}}$). We refrained from discussing this stage of the experiments because the cells and procedures we have used are not well suited for making quantitative measurements in this region. Inevitably, therefore, interpretations are speculative. There is no doubt, however, that stage 5 is probably the most interesting part of the experiments in that it points towards new systems which merit investigation. Suffice it to say that energies in the range observed are not within the realm of any chemical explanations.

Conclusion. Apart from the general description of stages 1–5, we find that the comments made by Morrison are either irrelevant or inaccurate or both.

References

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