EIGHT CHEMICAL EXPLANATIONS OF THE FLEISCHMANN–PONS EFFECT

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Abstract—Eight possible explanations for the heat produced in the Fleischmann–Pons effect are examined with the various conservative assumptions concerning the quantities used. No individual explanation is sufficient to explain the heat produced. All of them together can only explain heat as much as 3 W cm^{-3}.

INTRODUCTION

The Fleischmann–Pons Effect [1], in which electrochemical confinement of deuterium is said to give rise to heat production beyond that normally calculated, is based, in its experimental aspect, upon measuring the heat output from an electrochemical cell and comparing it with the electrical power put in.

The normal heat output of an electrochemical cell is (in W):

$$(E - 1.54)I \qquad (1)$$

where E is the potential applied to the cell in V and I is the current in A.

One of the ways in which the experiment may be carried out is to introduce an ohmic resistor into the solution to make a calibration graph. One passes a certain current through the resistor generating a known flux of heat. One allows the cell to attain steady state (~ 1 h depending on cell size and geometry) and obtains a point which indicates that the input watts give a certain steady temperature difference with respect to a constant temperature bath surrounding the cell. Eventually one gets a plot, shown in Fig. 1.

One can then monitor the performance of an electrochemical cell and if the cell, at an output of power calculated by equation (1), produces a temperature in the cell greater than that corresponding to the line in Fig. 1, one knows that there is an excess heat (which can then be measured by the displacement of the point from the ohmic heater established line).

Equation (1) is easy to test. If one utilizes a deuterium–oxygen cell consisting of platinum electrodes and an alkaline solution, one obtains precisely the heat output which is predicted by the formula. Because of the announcement of the Fleischmann–Pons effect in March 1989, many such tests have been made. The value of the thermoneutral potential given here is 1.54 V, for the electrolysis of D$_2$O. (For the electrolysis of water the corresponding value is 1.47 V.)

The palladium–hydrogen and palladium–deuterium system is well known, and subject to many complexities. It has been studied by F. Lewis [2], B. Flannigan [3], and more recently by M. Enyo [4].

In this paper, explanations of the Fleischmann–Pons Effect which are not based upon nuclear processes are examined. According to Fleischmann and Pons [1], their effect is able to produce ~ 26 W cm^{-3} for up to 1000 h. Somewhat lower excess heat, in the range from ~ 5–20 W cm^{-3} has been observed by others [5–7]. To stress a conservative stance, the chemical explanations put forward here will be compared with 20 W cm^{-3} for 50 h.

Explanations examined here may be by no means exhaustive but will serve as an introduction to a discussion of whether there are any numerically sound chemical explanations.
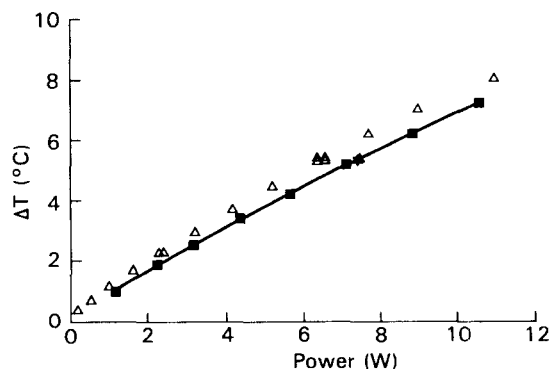

Fig. 1. Temperature difference between the cell and the constant temperature bath as a function of input power into the cell: ■—with electrical joule heater; △—charged Pd electrode in 0.1 M LiOD solution when excess heat was produced; ✳—charged Pd electrode in 0.1 M LiOD solution, when excess heat ceased.

EXTRA HEAT DUE TO THE LOSS OF COVERAGE OF THE ELECTRODE AND ITS CONTACT WITH THE DEUTERIUM–OXYGEN MIXTURE AT THE TOP OF THE VESSEL

The palladium rods are subjected to prolonged charging, at about 60 mA cm^{-2}, and then held at about 600 mA cm^{-2} for a time which may be as much as 20 h before the excess heat starts to show. The time during which the heat lasts is as low as 1 h [8] and as high as 1000 h [1].

Under conditions in which the palladium electrode contacts the deuterium oxygen mixture there will be a tendency of deuterium to come out of the electrode and react with the one-third atmosphere of oxygen prevalent in the deuterium oxygen mixture which is the gas with which it is in contact. In the solution, the electrode is wet and the adherent aqueous film will be taken as rate-determining the access of O_2 to the electrode.

The rate of pumping of D from bottom to top may be calculated as follows. Let it be firstly inferred that the rate-determining step is diffusion of D$^+$ in the Pd.

Velocity of D degassing under solid state diffusion control = $D_D c_0/r$ (moles cm^{-2} s^{-1}) [9], where $D_D =$ 10^{-6} cm^2 s^{-1} (for the β phase of Pd–D system) and c_0, the lowest value of D/Pd is 0.7, while the highest can be as high as 6 [10]. Then $(6 + 0.7)/2 = 3.3$ moles of D per mole of Pd.

This is clearly an abnormally high value, but we seek to be conservative, i.e. to make parameter choices which will tend to give the highest effect.

As the density of Pd is 12 and molecular weight 106, the molecular volume of Pd = 106/12 = 8.8 cm^3.

∴ Moles per cm^3 of D = 3.3/8.8 = 0.375.

∴ The heat production rate, per unit area, is

$$10^{-6} (0.375/0.2) (68.10^3/2) 4.18 \text{ J s}^{-1} \text{ cm}^{-2}$$
$$= 0.27 \text{ W cm}^{-2}.$$

∴ If area exposed is 1.25 cm^2 (i.e. 10% of the area of an electrode with diameter = 0.4 cm and length = 10 cm), the amount of excess heat = $0.27 \times 1.25 = 0.34$ W = 0.27 W cm^{-3} of the total electrode.

As stated, a likely rate-determining step is diffusion of O_2 through a liquid film on the emergent electrode. Such films are commonly found (cf. corrosion through moisture films [11]) to be 1 μ thick. Then:

$$i_L = \frac{D_{O_2} c_{O_2} F}{t} = \frac{10^{-5} \times 10^5 \times 2.2 \times 10^{-6}}{10^{-4}}$$
$$= 22 \text{ mA cm}^{-2}.$$

The rate of heat production for the electrode concerned =

The above calculation shows that for an electrode of 0.4 cm diameter, the excess heat produced by partial (10%) exposure of the electrode is rather small, for either of the rate determining steps assumed. However, the relative contribution may be significantly higher for smaller electrodes (because of the inverse dependence on radius and the smaller excess heat due to the lower volume), and for diameters of electrodes less than 0.1 cm, could become comparable with the reported excess heat. Hence, keeping the deuterium oxide above the electrode is then a most important aspect of the experiment! The question comes, of course, as to whether workers who have reported excess heat with smaller electrodes, have indeed kept their electrodes always totally immersed in deuterium oxide. There is during the experimental procedure a topping up of the electrolyte which always has to occur to avoid this, the deuterium oxide being used up by evaporation and by electrolysis. It is therefore important to notice whether a *sporadic decrease* of heat occurs after each topping up. For example in the work of Srinivasan *et al.*, no such changes were observed and the excess heat is constant over >80 h (being then interrupted by intended change of condition).

However, it is possible that such a situation has occurred and it is important that any experimenter is diligent in making quite sure that the deuterium oxide level never approaches the top of the electrode.

RECOMBINATION OF DEUTERIUM AND OXYGEN IN THE GAS PHASE

The combination of deuterium and oxygen, which is evolved from the concentric cylinder rod with its surrounding anode, will give rise to heat. The deuterium and oxygen bubbles would certainly be in sporadic contact in the solution before reaching the gas phase. From the qualitative point of view, one cannot say how much recombination takes place but intuitively one would expect little because in this model the deuterium and oxygen do not come in contact with a catalyst.

This "little" is easily confirmed by measurements of the amount of deuterium and oxygen evolved. The measurements of the volume of gases corresponds within ±2% to what one might expect on Faraday's law without recombination.

Now each mole of hydrogen, when it recombines with half a mole of oxygen to form water, evolves 68 kcal.

Thus for an electrode with 0.4 cm diameter and 10 cm length, the area is 12.5 cm^2 and the volume 1.25 cm^3.

Let us say that the current density during the process in which it is giving out heat is 1 A cm^{-2} so that the amount of D$_2$ produced is $12.5/2 \times 10^5$, i.e. 6.3×10^{-5} moles s^{-1}.

$$\frac{\text{Rate when the current is limited by } O_2 \text{ diffusion}}{\text{Rate when the current is limited by solid state diffusion}} \times \text{Calculated heat} = \frac{22}{150} \times 0.27 = 0.04 \text{ W cm}^{-3}$$

where 150 mA cm^{-2} comes from $(D_D c_0/r)F$.

Hence the heat being produced is $6.3 \times 10^{-5} \times 68 \times 10^3 \times 4.18$ J s^{-1} = 18 W or 14.4 W cm^{-3} which corresponds to the heat flux if all the D$_2$ combine with all the O$_2$.

If we assume a more reasonable 2% recombination, then we find that the heat produced by recombination would be equal to $14.4 \times 0.02 = 0.29$ W cm^3.

Thus, an explanation of the heat being produced on the basis of the homogeneous deuterium–oxygen recombination can be rejected completely.

OXYGEN–DEUTERIUM RECOMBINATION ON THE IMMERSED ELECTRODE SURFACE

A version of the above (illicit) heat source could occur if the bubbles which originate from the anode are impelled against the cathode. In this case there would be many bubbles during this and a significant effect would exist at all times and not be subject to the topping up phenomenon. Thus, it would be consistant with a constant heat.

Again assuming that 2% of the gases produced are consumed in the recombination, the amount of excess heat is 0.29 W cm^{-3}.

The contact time of each bubble with the palladium would be about 2 μs [12]. During this time deuterium on the electrode may react with O$_2$ from a bubble. Any reaction of this type would give rise to loss of oxygen. Experimental work done so far on this indicated that at least 99% of the expected oxygen arises.

HEAT FROM THE α TO β TRANSITION

There is a heat change in the lattice between the α and β phases for the palladium–deuterium systems. Let it be assumed that the change goes on slowly throughout the lattice so that it is still taking place after 50 h. Now, the heat of transformation between α and β is 33.6 kJ per mole of D$_2$ [13]. In the β phase the concentration of D in Pd is 0.7. Thus, the energy release per mole of Pd is 23.52 kJ, which corresponds to 0.13 W. As the molecular volume of Pd is 8.8 cm^3, the heat generated would be 0.015 W cm^{-3}. Compared with 20 W cm^{-3} this is negligible.

*Stimming [10] has suggested that the number could be 6. This is based upon the low temperature experiments. He evolved hydrogen on palladium at liquid nitrogen temperatures and because his electrolyte was frozen assumed that no gas bubbles could be formed and thus all went into the palladium. This seems an unlikely assumption.

†In most of the metal–hydride systems, energy has to be supplied to the system to release hydrogen (endothermic reaction). Thus, from this observation one would expect that if D$_2$ was released from the Pd lattice, the cell temperature should decrease rather than increase.

‡(2 × Energy in kcal × 1000 × 4.18)/(8.8 × 50 × 60 × 60).

D/Pd RATIO

Let it be assumed that during the charging of the metal the D/Pd ratio builds up until it reaches a value as high as 6 deuterium per palladium. The highest observed number has been 1.25, but the extra pressures given here by a high overpotential may lead to very high numbers.*

The value of the D–Pd bond strength was calculated from the value of the Pd–H bond strength (65 kcal mol^{-1} [14]) under the assumption that the Pd–D bond strength is ~15% higher, i.e. 75 kcal mol^{-1}. If this energy is released during 50 h for which the heat production has been reported the amount of excess power released is shown in the following table for different values of D/Pd.

Table 1. Calculated energy released as a function of D/Pd ratio

D/Pd ratio	0.7	1	3	6
Energy released (W cm^{-3})	0.14	0.2	0.6	1.2

PALLADIUM DEUTERIDE: PAULING'S THEORY

According to Pauling [15], during the charging process palladium deuteride (PdD$_2$) is formed and then dissociates (the author suggests, perhaps explosively) releasing heat.

Studies of H$_2$ in palladium show that no PdH$_2$ is formed [2]. The idea of an explosion occurring in a solid consisting of a metal with only ionic deuterium seems unreasonable. Furthermore, the situation would be going in the wrong direction because there is a concentration gradient, driving D inwards. Upon turning off the current the situation would be different and then something of what Professor Pauling says might occur.

However, if the heat stored in PdD$_2$ is released† slowly over a period of 50 h, the contribution due to this may be calculated as follows.

From the above discussion the bond energy for Pd–D bond is 75 kcal mol^{-1}. The lattice energy, calculated from the known value for the Pd–H system, for D in Pd is ~265 kcal mol^{-1} [16]. The contributions from the bond and lattice energies then come out to be 0.4 and 1.4 W cm^{-3}, respectively.‡

LITHIUM ALLOY FORMATION

If during the charging process Pd reacts with Li and forms a bond some energy may be released. This energy may be calculated from the knowledge of the bond strength of the Pd–Li which was calculated as follows [17]:

$$E_{Pd\text{-}Li} = (E_{Pd\text{-}Pd} E_{Li\text{-}Li})^{1/2} + 23.03 (\chi_{Pd} - \chi_{Li})^2$$

With $E_{Pd\text{-}Pd} = 33$ kcal mol^{-1} [18], $E_{Li\text{-}Li} = 26$ kcal mol^{-1} [18], $\chi_{Pd} = 2.2$ eV and $\chi_{Li} = 0.98$ eV, $E_{Pd\text{-}Li} =$

Table 2. Excess energy release due to different chemical processes

Chemical explanation	Energy released $(W\,cm^{-3})$
Partial exposure of electrode	0.04
Gas phase recombination	0.29
Surface recombination	0.29
$\alpha-\beta$ phase transition	0.015
D/Pd ratio: chemical storage	0.30
PdD_2 dissociation	1.8
Pd–Li formation	0.16
Stress release	0.10
Total (if all operating simultaneously)	3.00

$63.57\,kcal\,mol^{-1}$, which corresponds to $0.16\,W\,cm^{-3}$, much less than the measured excess heat.

In an alternate process one may argue that during the cathodic polarization of Pd electrode, Li is deposited on the surface. As compared to D_2 evolution, Li deposition takes place at $-3.045\,V$ [16]. Thus, in a cell where the cathodic reaction is deposition of Li and anodic O_2 evolution, in the first approximation, the thermo-neutral potential will be $1.54 + 3.045 = 4.585\,V$. This will result in cooling of the cell as compared to the D_2–O_2 evolution. If the deposited Li reacts with D_2O, heat will be released, thus, bringing back the temperature. However, if part of the Li goes into the lattice, all the energy will not be recovered. Thus, the process of deposition of Li will lead to consumption of energy, rather than release of energy.

RELEASE OF STRESS

During the process of charging of Pd electrodes with D, as D diffuses in, the Pd lattice is stressed. These stresses may accumulate over a period of time leading to propagation of small cracks through the metal. If the lattice relaxes at a later time, the stored stress energy may be released.

The total energy of internal stress $= E\eta$ where E is Young's modulus $(= 1.21 \times 10^{12}\,dyn\,cm^{-2})$ [19] and η is the total relative volume change during the charging process $(= 0.15)$. Again, if this energy is released over 50 h:

Excess power $= (1.21 \times 10^{12} \times 0.15)/(50 \times 60 \times 60 \times 10^7) = 0.10\,W\,cm^{-3}$.

SUMMARY

In this paper, various happenings which could be considered to be occurring during the experimental work are considered.

On the basic assumption that heat is observed for several tens of hours, and that the order of magnitude of this heat is $20\,W\,cm^{-3}$, no one explanation will suffice to explain the magnitude of the heat observed for the time stated.

Were all the explanations added and all to apply, then it would be possible (Table 2) to reach the lower ranges of the heat sometimes observed, i.e. when the heat is observed to be as low as, say $3\,W\,cm^{-3}$.

On the other hand, the simultaneous occurrence of all the causes mentioned here is extremely unlikely. There are other aspects which seem to make chemical explanations improbable.

The first, of course, is the case where the amount of heat produced has been observed to pass the break-even characteristic, i.e. that more energy is produced in the form of heat than has been put in the form of electricity. There would be no possibility of explaining this on a long-term basis.

Another aspect concerns the fact that these effects are only observed in the presence of deuterium. Corresponding experiments with hydrogen did not give rise to any of these phenomena.

Finally, the presence of tritium in the solution [20] suggests that a nuclear process is occurring, although it is true that a direct connection between the production of heat and the production of neutrons has not occurred.

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