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REPORT ON COLD FUSION EXPERIMENTS

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Contents

General Introduction

On the 23rd of March 1989 Martin Fleischmann and Stanley Pons of the University of Utah in Salt Lake City (U.S.A.) declared in a press conference that they had discovered a new source of energy for the future: cheap, easy, clean and unlimited. They went on to describe summarily their experiments involving electrolysis of heavy water (D_2O) using a palladium electrode. The process generating energy supposedly was nuclear fusion that occurred in the palladium electrode, saturated with deuterium.

The lack of detail in the description of the experiment did not stop their colleagues from attempting to reproduce the feat. In doing so they had to speculate about the most proper way to set up the experiment and the e-mail circuit was bustling with communication on the subject.

Meanwhile the press had gotten hold of the topic and was pressing the various large laboratories in the world to give their opinion on the subject. Many laboratories decided to make a team of investigators available for a reproduction experiment. Some teams of workers could not resist the temptation of publicity and prematurely presented successful results that had to be retracted subsequently. The English laboratory Harwell was asked by Fleischmann to verify his claims, but both they and Fleischmann kept silent initially.

In the middle of all the excitement there was another claim, made by Steven Jones from the Brigham Young University in Utah. His research also involved the electrolysis of heavy water but he focused on the production of neutrons, using advanced neutron counting equipment. The rate of fusion reactions he claimed to be observing, however, was 10^4 times less than that of Fleischmann and Pons, and was considered to be more realistic.

In the Netherlands the excitement was no less. On the 4th of April a 'brainstorm'-session was held at the Instituut voor Plasmafysica 'Rijnhuizen'. All Dutch research groups that were involved as well as some individuals were represented. Tasks were divided between the various institutes and groups, each working within his own specialism [1, 2, 3], except the Institute for Plasma Physics itself that did not possess any related specialism but had a keen interest in nuclear fusion. The resulting cooperation was exemplary. Knowledge, material, equipment and manpower were shared enthusiastically.

As the Dutch research projects advanced and failed to verify the claims, the world scientific community likewise became more sceptical. Various serious mistakes in the experiments presented by Fleischmann and Pons were discovered. The Harwell Laboratory, using some of the best possible equipment and the original 'fusion cells' also used by Fleischmann and Pons reported negatively on their reproduction efforts. Before summer the dream was over and hardly anyone believed the original claims.

This report is presented in part as a historical document, reflecting the excitement felt in the physical community at the time of the 'cold fusion' craze (see also [4, 5, 6]). In part it is presented as a record of some unusual experiments and of the very inspiring cooperation between various institutes and universities.

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Part I: Electrolysis and calorimetry at Rijnhuizen

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Abstract

Several electrolysis experiments were carried out at the FOM Institute for Plasma Physics. Calorimetric measurement of heat production during electrolysis of D_2O with a number of Pd cathodes was performed. Prior to electrolysis the Pd was loaded with H or D in an especially developed gas oven. No evidence of anomalous heat production was found.

1 Introduction

At the press conference given by Fleischmann and Pons (FP) on 23 March 1989 and in their subsequent publication of experimental results in the Journal of Electroanalytical Chemistry [1], extraordinary observations of abnormal heat and neutron production in a simple experiment were reported.

Severeal electrolysis experiments, designed to verify the claims of large heat production, were carried out at the FOM Institute for Plasma Physics in collaboration with the Interfacultary Reactor Institute of the University of Delft and the Van 't Hoff Laboratory of the University of Utrecht.

A pilot experiment, involving calorimetric measurement of heat production during electrolysis of D_2O with a Pd cathode, was initiated on March 25. It was operated with a number of different electrodes. A second experiment was carried out with more sophisticated equipment and large Pd cathodes that were subjected to special treatment before use.

2 Experimental design

Shortly after the first unsuccessful attempts at reproducing the remarkable heat and neutron production, people speculated about a special treatment to which the Pd electrodes should be subjected prior to use. From the scanty publications about cold fusion [1,2] it was not clear what this pre-treatment should be. The hypothesis that gas would collect under high pressure in cavities in the Pd electrode was rejected because such cavities would collect hydrogen or deuterium in the gas phase, in which no fusion will occur. Therefore it was decided to avoid creating lattice deformations and cavities in the samples of the concluding experiment. In our pilot experiment we used simple Pd wires that were annealed, but in the concluding experiment we used cast and annealed Pd (Table I.1).

Table I.1	Pd electrodes			
Experiment	Run	Pd electrode		
		Length	Diameter	Remarks
Pilot	1 through 5	25 cm	1.8 mm	Annealed
Pilot	6 through 10	4.02 cm	4.0 mm	Annealed
Concluding		2.5 cm	6.0 mm	Cast and annealed 2 identical electrodes

In accordance with a rough sketch of the experimental set-up of FP obtained by fax, the first five pilot experiments (Table I.1) were carried out with a long Pd electrode that emerged above the electrolytic fluid. This set-up, however, does not facilitate a proper evaluation of the power balance due to recombination of the D_2-O_2 gas mixture to D_2O at the Pd surface, which catalyzes this exothermal reaction. Also, D may diffuse through the Pd electrode and recombine outside the electrolytic cell, thus heating the cell by an unknown amount. Therefore we used a shorter electrode in our second series of pilot experiments (runs 6 through 10), such that the Pd was completely immersed.

When electrolytically charging Pd with H or D, the Pd-H or Pd-D system passes through a two-phase region [3,4] (Fig. 1). The transition from the α to the β phase is accompanied by an increase in the lattice constant (from $a = 0.3890$ nm to $a = 0.4025$ nm at room temperature [4]) and lattice distortions. The phase transition can be avoided, and thus
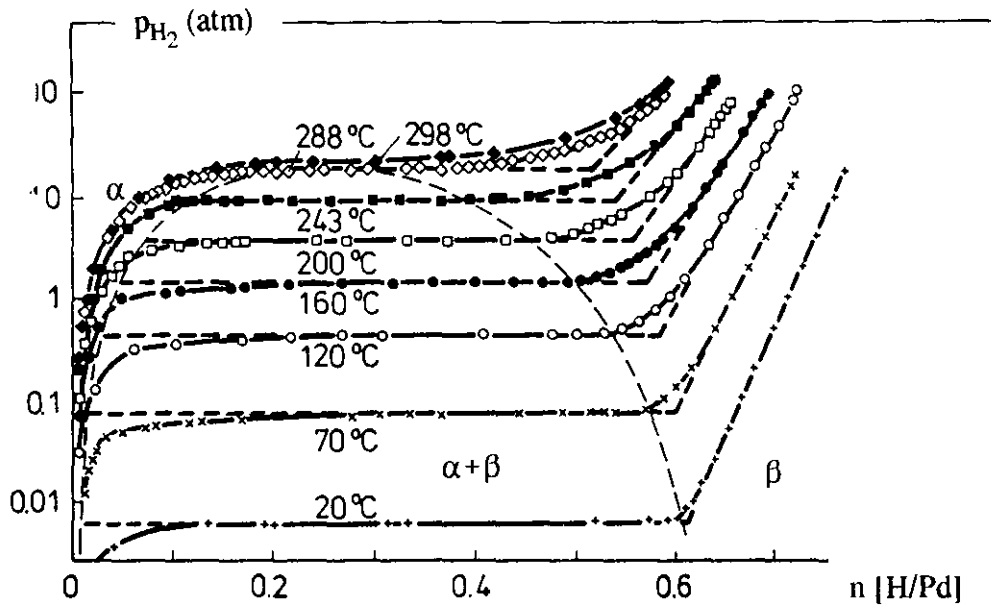
Fig. 1.   Phase diagram for the Palladium-Hydrogen system [3]. The two phases α and β as well as the two-phase region α+β are indicated.

lattice homogeneity preserved, by loading the Pd with H or D above the critical temperature, i.e. 300 °C. Obviously, this cannot be done in electrolysis. Therefore a gas oven was constructed in which the Pd electrodes were pre-loaded to $n = n_H/n_{Pd}$ or $n_D/n_{Pd} = 0.6$ at temperatures around 400 °C and H_2 or D_2 gas pressures around 100 bar. Afterwards temperature and pressure were lowered. This procedure was applied to all experiments from run 6 onwards.

To obtain fusion, the D atoms must be brought close together. Therefore the loading factor (n) was maximized in the experiment. The value of n that can be reached in electrolysis (0.8 - 0.9) depends on the over-potential that can be achieved at the electrode surface [4]. This potential can be maximized by using a very smooth electrode surface. At the same time, at such a smooth electrode surface the formation of gas bubbles is suppressed, which also leads to higher potentials. The electrodes used in the concluding experiment were smoothened by softly hammering the surface.

The pilot experiments were carried out in a single electrolytic cell that was calibrated by operating the electrolysis with the current in the reverse direction or by exchanging the heavy water for ordinary water. The concluding experiment consisted of two identical electrolytic cells connected in series, one with heavy water and one with ordinary water, that were separately calibrated.
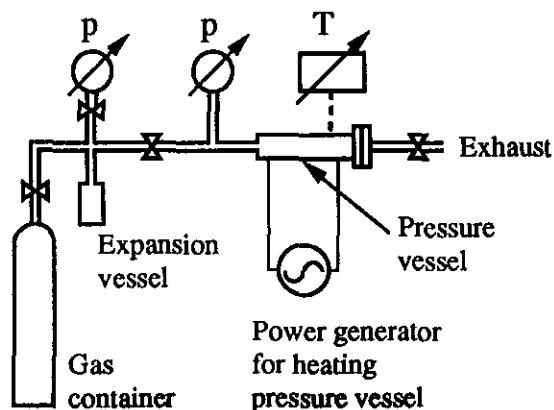
Gas loading set-up

Fig. 2.   Schematic view of the gas loading set-up. Pressure meters are indicated by 'p'; temperature meters by 'T'. The pressure vessel can be opened on the right-hand side to insert the Pd rod. The pressure vessel is heated by passing a large alternating current through the vessel wall. The temperature of the vessel is monitored with a thermocouple.

3   Experimental set-up

3.1   Gas loading set-up

A schematic of the gas loading set-up and a photograph of the actual set-up are shown in Figs. 2 and 3. The set-up was tested by inserting annealed Pd, by first heating the gas chamber to 450 °C, and then admitting H_2 gas at 100 bar pressure. After 15 minutes the gas chamber was cooled to room temperature. The gas pressure was reduced to 1 bar and the Pd sample was extracted. The length and weight of the sample (both indicators of the loading factor n) were measured and compared to the corresponding values before onset of the experiment. Both measurements revealed consistently that the H loading factor of the Pd sample was 0.60 ± 0.05. This result was sufficient for our purposes, as we had thus successfully passed the two-phase region.

3.2   Pilot experiments (runs 6 through 10)

The electrolytic cell of the pilot experiment consisted of a glass cylinder (2 cm inner diameter and 20 cm in length) with the Pd electrode centered and the Pt electrode wound around it in a helix. A sketch of the experimental set-up is shown in Fig. 4. The temperature of the electrolyte was measured by three Chromel-Alumel thermocouples placed in a glass capillary outside the Pt helix. To ensure good heat conduction to the thermocouples the capillary was filled with paraffin. Another glass capillary allowed the produced gas (D_2 or H_2 and O_2) to escape from the cell and permitted replenishment of the electrolyte. A silicone tube connected to this capillary outside the cell led the escaping gas through a waterlock, and to a set-up where the gas flow could be measured.
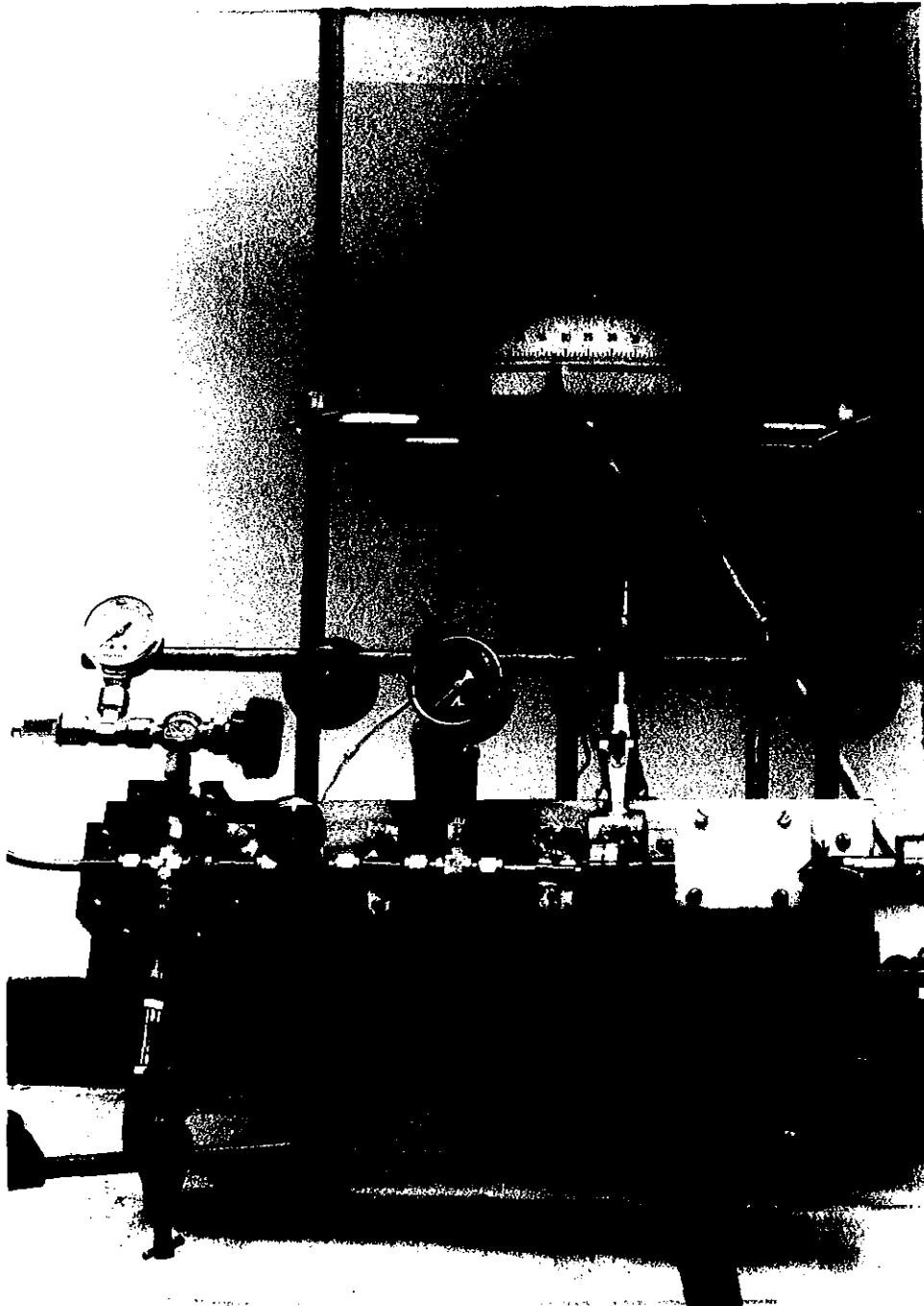
Fig. 3.   *Photograph of the main part of the gas loading set-up schematically shown in Fig. 2.*

Pt electrode

Pd electrode

thermocouples

D₂ and O₂

D₂O

air

glass tube

gold wire

ceramic bead

Pt electrode
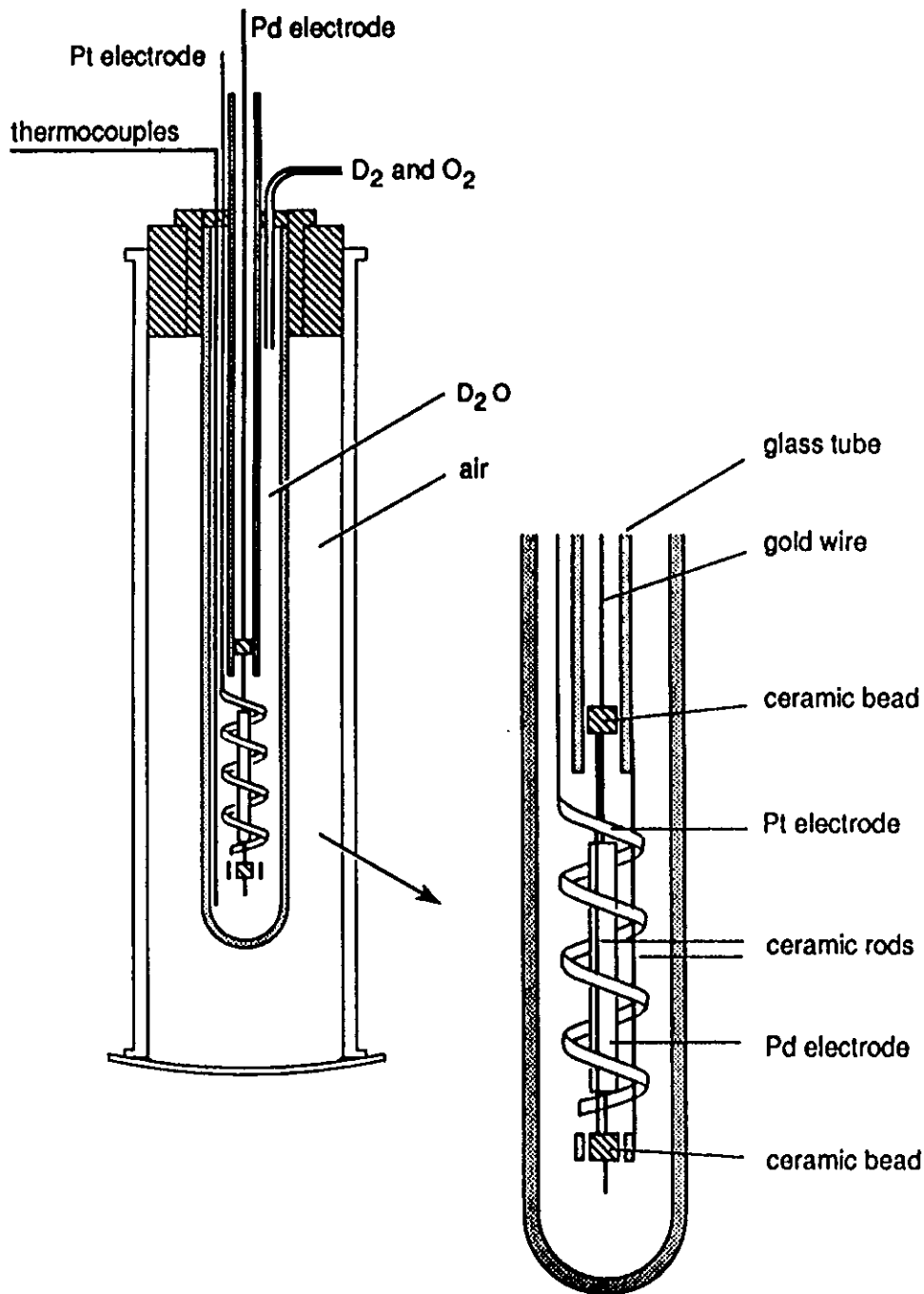
ceramic rods

Pd electrode

ceramic bead

Fig. 4. Schematic view of the electrolytic cell used in the second set of pilot experiments (runs 6 through 10). The inner test tube is isolated from the outer tube by means of air. The inner tube contains the electrolyte (indicated by D₂O). The Pd electrode can be removed from the experimental set-up through the innermost glass tube. The ceramic beads and rods are included for positioning and stability purposes.

The Pd connection lead entered the cell through a long narrow glass tube (5.0 mm inner diameter). The platinum electrode, a thin (0.2 mm) 2.2 mm wide strip, was wound on a cage made out of three thin ceramic rods, 7 cm long, connected to the mentioned glass tube. The Pd electrode was inserted into the cell by lowering it through this glass tube. It was held in position by two ceramic centering beads that were fixed on gold wires (1.0 mm diameter) connected to the electrode on both ends: a long connecting lead at the top and a short (1 cm) piece, needed for centering, at the bottom of the electrode. Where the gold wire left the glass tube a seal was present to prevent gas from escaping the cell.

This entire cell was placed in a larger glass cylinder with an inner diameter of 5.2 cm and a length of 25 cm. The space between the cell and this cylinder was filled with air and insulated the cell from the water bath that surrounded the cylinder. Both the cell and the surrounding cylinder were closed at the top with caps made out of PVC. The water bath was kept at a constant temperature (25 ± 0.1 °C) by a thermostat. Cell voltage, current and temperature were recorded with paper writers.

3.3 The concluding experiment

The experimental set-up is schematically shown in Fig. 5. A photograph is shown in Fig. 6. Two identical electrolytic cells were installed in an isolated box. The initial molarity of the electrolyte was 0.5 M LiOD, resp. 0.5 M LiOH. Two Pd electrodes on gold leads, pre-treated as described in Section 2, were mounted in the centre of the cells, nearly touching the bottom to improve fluid temperature homogeneity. The fluid was stirred by the gas bubbles produced in electrolysis. The Pd electrodes were surrounded by helically wound Pt counter-electrodes. The cells were connected in
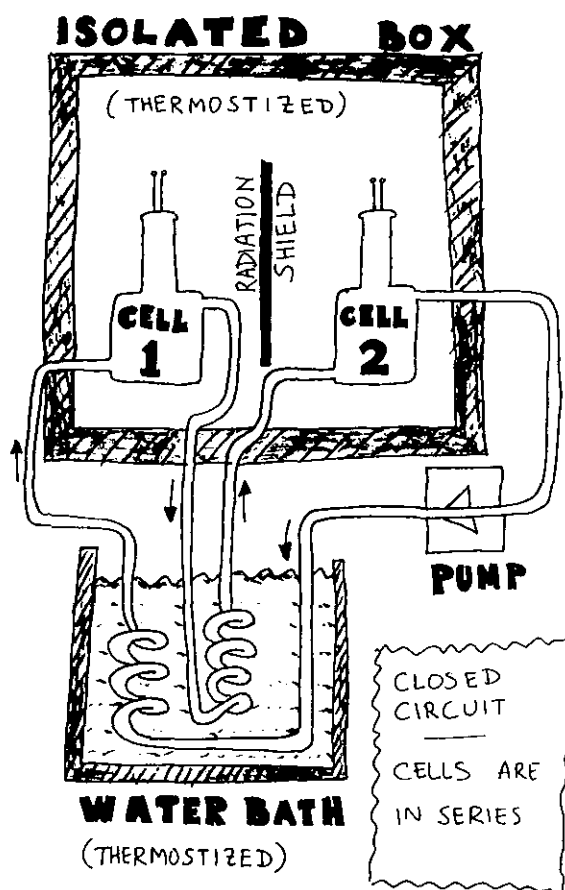

Fig. 5.   Schematic of the set-up of the concluding experiment. The cells are cooled with water that is kept at a constant temperature in a closed circuit such that the cell mantles are in series.

series to a power supply, in order that the amount of current flowing through one cell would also flow through the other. Cell voltage was measured at the electrode leads directly outside the cells. Current was measured by recording the potential drop across a reference resistor.
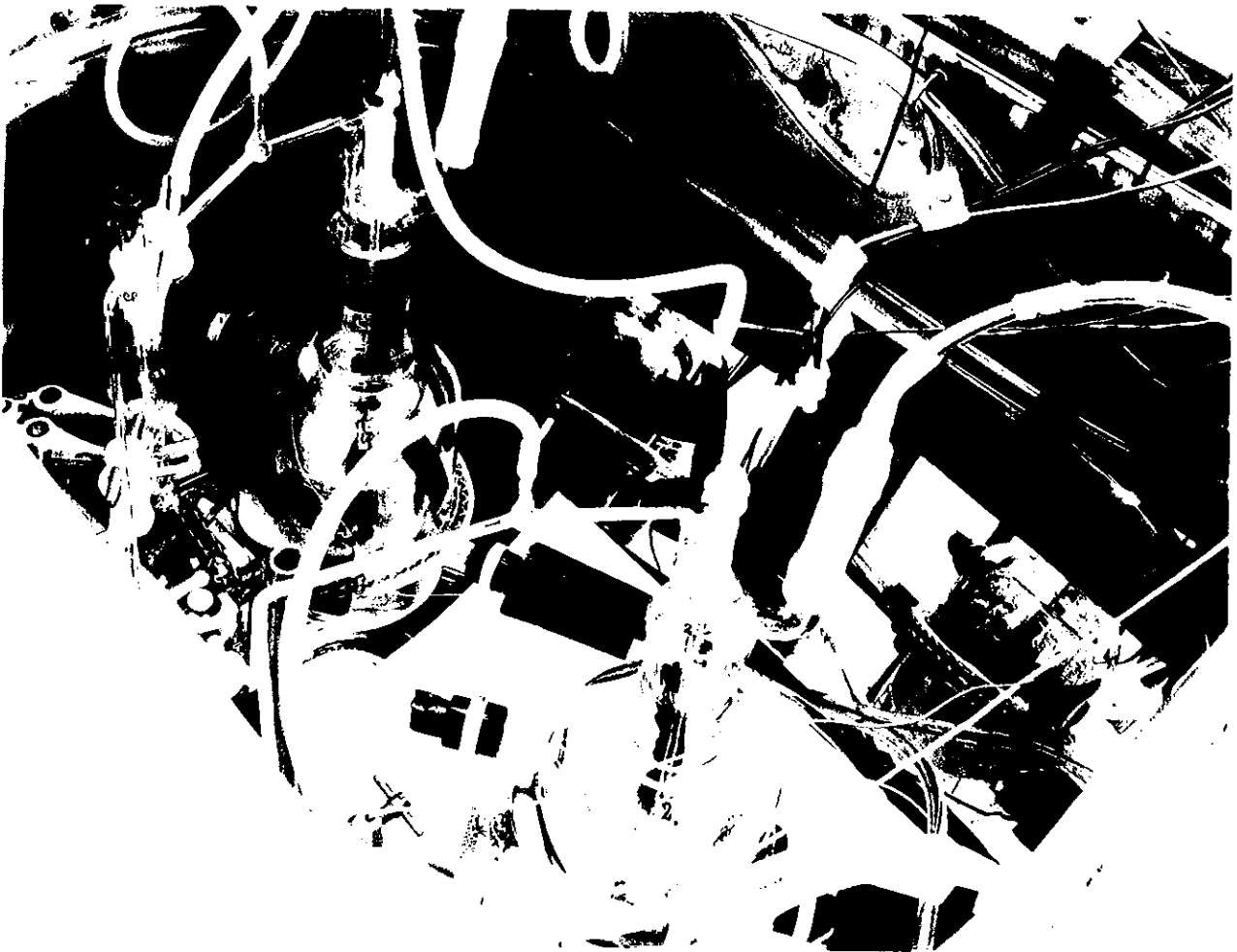

Fig. 6. *Picture showing the experimental set-up of the concluding experiment. The two cells can be seen with their respective gas outlets, electrode connections and salt bridges. The mirrors are used for monitoring the water level. The radiation shield has been removed for the picture.*

Both cells were kept at an approximately constant temperature by means of a cooling water mantle. The cells were connected in series to a water pump, such that the water flow speed would be the same for both cells at all times. Before entering the water mantle of a cell, the water would pass through a thermostat bath and be led through tubes of equal length, such

that any influence of the thermostized box on the water temperature would work out identical for both cells, and the inflowing water would have the same temperature for both cells. The temperature difference of the outflowing and inflowing water was recorded for each cell using Copper-Constantan thermocouples.

In both cells, a reference electrode (Calomel) was placed directly outside the Pt electrode. The temperature difference between the two electrolytes was monitored using Copper-Constantan thermocouples. Both cells were sealed from the outside world by a glass cap. An exhaust allowed the produced gas to escape. This gas was led through silicon tubes to a set-up where the gas flow could be measured and the explosive gas (mixed H_2 or D_2 and O_2) led away safely.

The temperature difference of the cooling mantles, the cell voltages, the current, the reference electrode voltages and the temperature difference between the two electrolytes were recorded by a computer. The box temperature was recorded by a paper writer. Water flow, gas flow and temperature of the thermostat bath for the cooling water were measured at regular intervals.

4 Experimental results

4.1 Pilot experiments (runs 6 through 10)

The second set of pilot experiments consisted of four runs, two of which were done for calibration purposes (see Table I.2).

Table I.2: Overview of pilot experiments

Exp. #	Period	Current	Electrolyte	Purpose
6	May 28	Pd cathode	LiOD 0.5 M	measurement
7	May 28 - 29	Pd anode	LiOD 0.5 M	calibration
8	May 29 - 30	Pd cathode	LiOH 0.5 M	calibration
10	June 2 -19	Pd cathode	LiOD 0.5 M	measurement

Experiment 9 is missing in this table because of a faulty set-up. A planned calibration run after experiment 10 was made impossible by an explosion in the test tube on June 19, probably caused by a spark in the explosive D_2-O_2 gas mixture.

Cell voltage V, current I and temperature with respect to the water bath T were monitored continuously by paper writers. At regular intervals, the gas flow out of the test tube was measured. By comparing this flow with the current I it was possible to note when the Pd electrode was saturated with H or D. The input power P* (Eq. I.1) was varied between 0.3 and 3 W in experiments 6 through 9, and kept approximately constant at 2.3 W in experiment 10. After a value of P* had been chosen, it took approximately one hour for an equilibrium or stationary state to establish itself. For each equilibrium we obtained, the following two quantities were computed:

Input power $\qquad\qquad P^* = I(V - V_0)$ $\qquad\qquad\qquad\qquad$ (I.1)

Corrected temperature $\qquad T^* = T(1 + \alpha\Delta\Omega),$ $\qquad\qquad\qquad$ (I.2)

where Ω is the electrolyte volume, $V_0 = 1.53$ V for H_2O and $V_0 = 1.58$ V for D_2O [5]. The temperature is corrected for the varying amount of electrolyte in the cell according to Eq. (I.2), which is derived from a first-order approximation to the change in heat capacity of the electrolytic cell due to a change in electrolyte volume. Every few hours, the amount of electrolyte was replenished with H_2O or D_2O to a fixed level Ω_0. $\Delta\Omega$ is the amount of electrolyte present in the cell minus Ω_0, and is proportional to the integral over time of the cell current. The geometrical factor α was experimentally determined from quasi-stationary states in which the depletion of the electrolyte volume was observed over a long period of time while keeping all other parameters fixed ($\alpha = (0.015 \pm 0.004)$ ml^{-1}).

In order to establish the equilibrium power balance equations, one must take both conduction and radiation losses into account:

$$P_{cond} \quad = \kappa \, (T{-}T_{env})$$

$$P_{rad} \quad = \sigma \, A_{eff} \, (T^4{-}T_{env}^4),$$

where κ is a proportionality constant, T_{env} is the constant temperature of the environment (the water bath), σ is Stefan-Boltzmann's constant and A_{eff} is the effective radiating surface of the electrolytic cell. These heat losses add up to a total power loss term (introducing $\kappa_{eff} = \kappa + 4\sigma A_{eff}T_{env}^3$, assuming T_{env} to be constant), taking only 1st and 2nd order terms in (T$-$T$_{env}$):

$$P_{loss} = \kappa_{eff} \, (T{-}T_{env}) + 6\sigma A_{eff}T_{env}^2(T{-}T_{env})^2 \qquad\qquad (I.3)$$

that should be balanced by P* (Eq. I.1).

For each run, T* was plotted versus P* (Fig. 7). The curvature in the lines is explained by Eq. (I.3). Note that in this figure experiment 6 does not differ significantly from the two
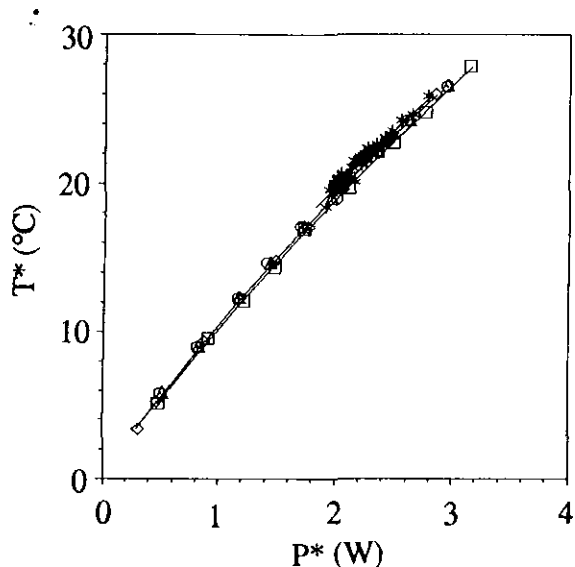
Fig. 7. *Graph of T* versus P*. The relationship between corrected input power and equilibrium temperature is nonlinear, as predicted by Eq. (1.3). Symbol table:*
O run 6   ◊ run 7
□ run 8   * run 10
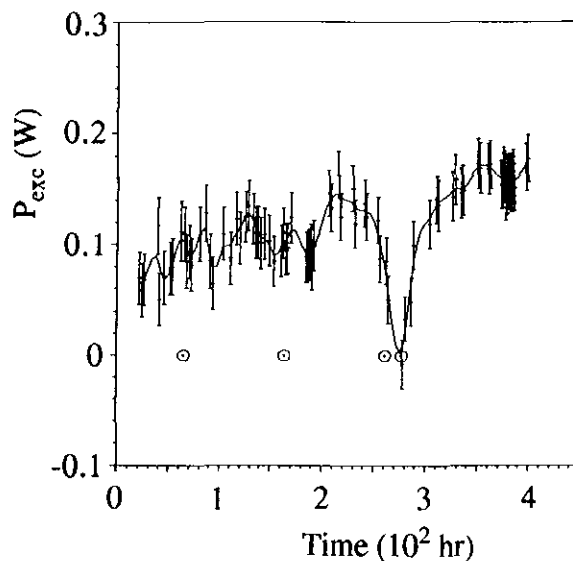*Note how little run 10 deviates from the calibration runs 7 and 8.*

Fig. 8. *Excess power according to Eq. (1.4) for run 10. O - symbols indicate temporary removal and cleaning of the Pd electrode. The excess power seems to decrease as the Pd electrode blackens, and to increase after cleaning. Note that it was not possible to recalibrate after termination of the experiment.*

calibration runs, whereas experiment 10, which was operated for over 400 hours, has on average lower P* at the same T* than the other runs.

Using run 8 as the definitive calibration, we made a plot of P_{exc}, the excess power, versus time for run 10. The excess power is defined as

$$P_{exc} = P_{cali}(T^*) - P^*,$$ (1.4)

where $P_{cali}(T^*)$ is P* belonging to T* as determined from a quadratic fit to the data of run 8. The result is shown in Fig. 8. The error bars are estimates of our measuring accuracy due to instrumental errors and statistical errors in the calibration data. We see a gradual increase of P_{exc} with time to a maximum of 0.2 W, i.e. less than 10% of the input power. The Pd electrode developed a dark oxide layer after days of use, so at regular intervals the electrode was cleaned by taking it out of the electrolysis and wiping it clean with a soft cloth. The last time we did this, we used fine grain polishing paper. The decrease of P_{exc} coincided with the blackening of the electrode, and that the last polishing action was followed by a sharp increase in P_{exc}.

Nevertheless we are reluctant to interpret this result as a true excess heat, because we could not perform a calibration after termination of the experiment, due to the above-mentioned accident.

After run 10 the Pd electrode was removed from the experiment and quickly cooled to liquid nitrogen temperature. At the Interfacultary Reactor Institute in Delft the electrode has been analysed for the amount of deuterium it contained. Desorption spectrometry has shown that high deuterium densities had been achieved: n = 0.82 ± 0.03. Mass spectrometry has shown that the desorbed deuterium contained a small amount of hydrogen (97% of D_2 and 3% of HD): A peak at mass 3 was identified with DH and was found to be $\frac{1}{30}$ of the one at mass 4 (D_2). This amount of H (1.7 %) has probably entered the palladium through the electrolysis of D_2O. Although the D_2O employed was 99.9 % pure, the amount of D_2O used in the last run was rather substantial: 200-300 ml, and H has a larger affinity to Pd than D (separation factor n_H/n_D = 9 [4]).

The radioactivity of the electrolyte was determined to be 21 Bq/ml (unused D_2O) and 35 Bq/ml (used D_2O). The difference can be explained by the enrichment of T in D_2O during electrolysis due to isotope effects and must not be interpreted as an indication for fusion.

4.2 The concluding experiment

The heat balance in this experiment is quite complicated, as will be shown by the following argument. First of all, we have the input power:

$$P_{in}(i) = I \cdot (V(i) - V_0(i)) - I^2 R_{Pt}(i), \qquad i = 1,2 \qquad (I.5)$$

where the index i refers to the cell. By convention, i=1 denotes the cell with ordinary water and i=2 denotes the cell with heavy water. The cell voltage V(i) was measured at a point directly outside the cell. However, some power dissipated in the Pt and Au connectors between this point and the cell cap. R_{Pt} is the resistance of this part of the connectors. $I \cdot V_0(i)$ is the power needed for decomposition of the (heavy) water into hydrogen (deuterium) gas and oxygen. We used the tabulated values [5]:

$$V_0(1) = 1.53 \text{ V}$$

$$V_0(2) = 1.58 \text{ V}. \qquad (I.6)$$

There has been some confusion on the correct numerical values of these constants. These numbers have been computed from the heat of combustion of H_2 or D_2 and O_2 of 25°C at p = 1 bar to form liquid H_2O or D_2O of 25 °C. The electrical power dissipated in the electrolyte, as given by Eq. (I.5), is for the larger part transferred to the cooling water. If the water in the cooling mantle has a flow speed S [ml/min], and the temperature difference between the out- and inflowing water is $\Delta T(i)$ [°C], then the output power $P_{out}(i)$ is computed as:

$$P_{out}(i) = S \cdot \Delta T(i) \cdot c_w / 60, \tag{I.7}$$

where c_w is the heat capacity of water, $c_w = 4.19$ [J/(g $^\circ$C)].

However, the water in the cooling mantle also interacts with the air in the surrounding thermalized box through radiation. If the box is assumed to have a homogeneous temperature of T_{env}, and the cooling water has an average temperature of $T_w^{av}(i)$, then there is an additional power loss term P_w^{loss} that can be estimated by using Stefan-Boltzmann's blackbody radiation law and taking only linear terms into consideration, which is justified since the temperature difference $T_w^{av}(i) - T_{env}$ is small compared to the environment temperature in degrees K.

$$P_w^{loss}(i) = A_w^{eff}(i) \cdot 4\sigma T_{env}^3 (T_w^{av}(i) - T_{env}), \tag{I.8}$$

where $A_w^{eff}(i)$ is the effective radiating surface of the water mantles and σ is Stefan-Boltzmann's constant: $\sigma = 5.6703 \cdot 10^{-8}$ W/(m^{2}K^4) [5]. A similar power loss term, P_{cell}^{loss} results from radiation emitted from the electrolyte that does not deposit its heat in the transparent water mantle, but in the box. The radiating surface of the electrolyte varies with the amount of electrolyte present at each moment in time. In order to accomodate both these power loss terms, we define a total power loss term for radiation effects P_{rad}^{loss}:

$$P_{rad}^{loss}(i) = A_{rad}^{eff}(i) \cdot \left[1 + \frac{\Omega(i) - \Omega_0(i)}{\omega(i)} \right] 4\sigma T_{env}^3 (T_w^{av}(i) - T_{env}), \tag{I.9}$$

where $A_{rad}^{eff}(i)$ is the total effective radiating surface, $\Omega(i)$ is the electrolyte volume, $\Omega_0(i)$ a reference volume and $\omega(i)$ a geometrical factor that is to be determined experimentally. Even if there is a temperature gradient across the electrolyte, which there probably will be, Eq. (I.9) will give a good description of the behaviour of the system, because this gradient is purely geometrical and its effect is incorporated in the experimentally determined effective radiating surface.

A further loss term results from the evaporation of (heavy) water during the experiment. That water actually evaporates can be judged by the condensation in the exhaust gas tubes. We used a cold trap to roughly measure the amount of water evaporated while operating the experiment at maximum power input, and found that the evaporation of water contributes of the order of 1 mW of additional power loss, and therefore may be ignored, since we estimate our measuring accuracy at 100 mW with maximum power input (i.e. 20 W).

Equations (I.5), (I.6), (I.7) and (I.8) provide the detailed power balance of this experiment. It will be noted that the measured temperature difference of the cooling water $\Delta T(i)$ depends on *four* quantities: $P_{in}(i)$, T_{env}, T_w^{av} and $\Omega(i)$, assuming S to be constant. The quantity T_w^{av} is a bit awkward because it is not measured directly. However, it may be estimated by

$$T_w^{av}(i) = T_w^{in} + \tfrac{1}{2}\Delta T(i),\tag{I.10a}$$

where T_w^{in} is the temperature of the water as it enters the cooling water mantle of cell i. The cooling water is transported from the water bath to the cells through silicone tubes. The cooling water will change in temperature during transit from the water bath to the cells due to interaction with T_{env}, and T_w^{in} in Eq. (I.10a) can be estimated by

$$T_w^{in}(i) = T_w + \alpha(i)(T_{env} - T_w),\tag{I.10b}$$

where T_w is the temperature of the water bath in the cooling water cycle. The quantities $\alpha(i)$ can be determined by measuring the temperatures $T_w^{in}(i)$, T_w and T_{env} simultaneously in a calibration run.

The electrolytic cells are calibrated using a power resistor instead of electrolysis as the input power source. By varying the four parameters mentioned above, the quantities $A_{rad}^{eff}(i)$ and $\omega(i)$ are determined in order that the relationship $P_{in}(i) = P_{out}(i) + P_{rad}^{loss}(i)$ is satisfied. Of course the input power is now computed using $V_0(i) = 0$. Using this calibration, the excess heat of the experiment is defined as:

$$P_{exc}(i) = P_{out}(i) + P_{rad}^{loss}(i) - P_{in}(i).\tag{I.11}$$

This definition of excess heat provides a good check of the method, for it should always be zero for the cell with H_2O.

In the above description of the physical system we did not take into account the recombination of H_2 or D_2 to H_2O or D_2O. We have measured the gas flow leaving the electrolytic cells and found that it agreed with the electrical current flowing to within the measuring accuracy of 1%, while the overall measuring accuracy of the output power was near 5%, so recombination, in our case, could be ignored.

The calibration was carried out immediately after termination of the concluding experiment. The electrolyte was replaced by water, which does not influence the power balance, and the electrodes were replaced by power resistors. By varying T_{env}, while keeping $P_{in}(i)$ at around 5 W and Ω at 150 ml, the effective radiating surface was determined from a fit of the data to Eq. (I.9). We found

$$A_{rad}^{eff}(1) = 0.046 \pm 0.003 \text{ m}^2 \text{ and}$$

$$A_{rad}^{eff}(2) = 0.028 \pm 0.001 \text{ m}^2.$$

Note the large difference between the cells, which were nevertheless constructed to be nearly identical. We attribute this to different radiative characteristics of the immediate surroundings of the cells.
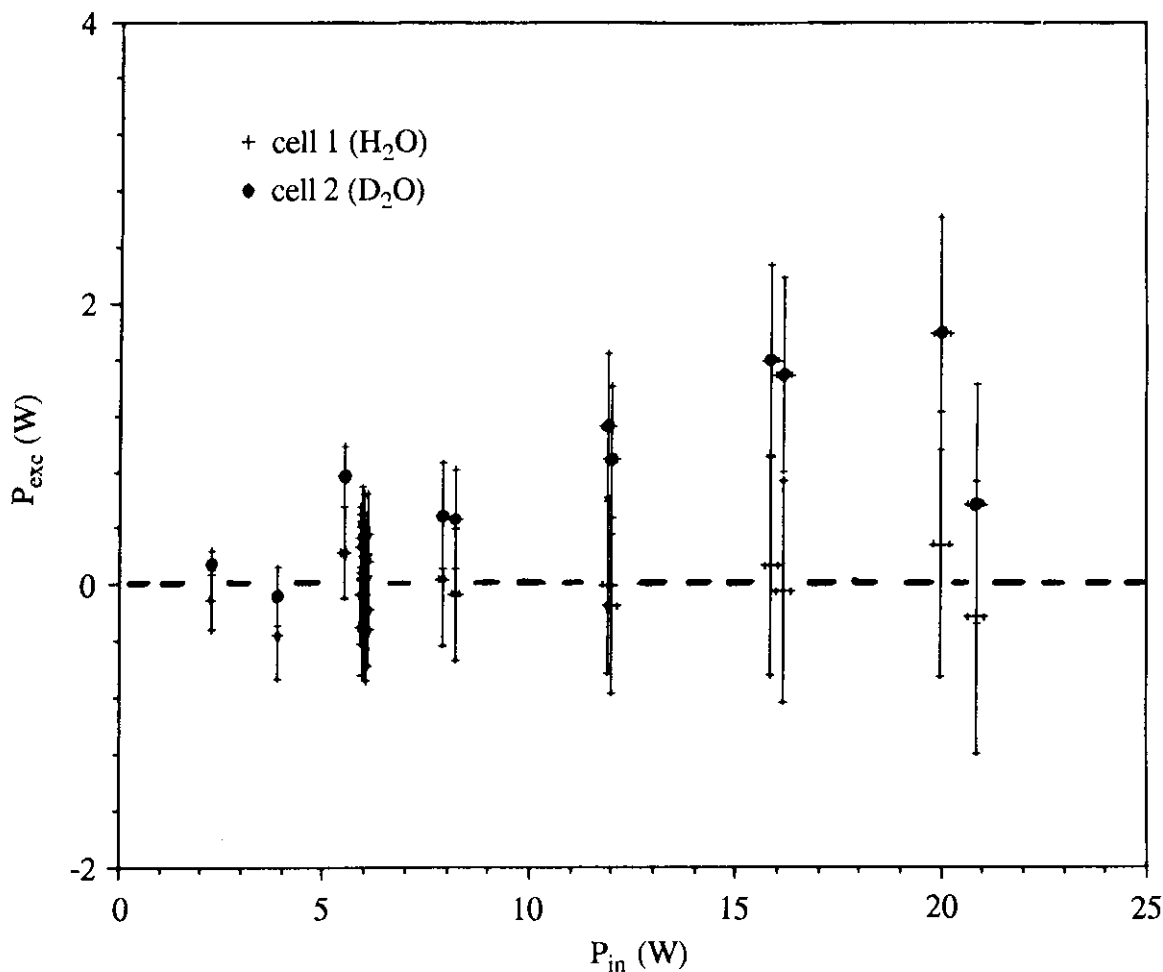
Fig. 9. *Excess power versus input power for the two cells in the concluding experiment. Cell 1 contains H_2O, cell 2 D_2O. The cells are independently calibrated. There is a small deviation from zero (< 10%) for cell 2 at high input power.*

From Eq. (I.10b) and the appropriate measurements the quantities $\alpha(i)$ were determined:

$$\alpha(1) = 0.133 \pm 0.005 \qquad\qquad \alpha(2) = 0.211 \pm 0.005.$$

We estimated the resistance of the connecting wires $R_{Pt}(i)$ and found

$$R_{Pt}(1) = R_{Pt}(2) = (0.07 \pm 0.01) \ \Omega.$$

This estimate assumes that the resistance of the connecting leads and a possible contact resistance was the same for both cells, which may not have been the case. We realized that this effect might play a role too late to be able to verify this. If this assumption errs by, say, 0.03 Ω,

then this might lead to an excess power that is wrong by 0.75 W at 5 A cell current, which is of the same order as some values of the excess power that were measured.

By varying the electrolyte volume we found that the effect of this on the radiative power loss was smaller than our detection limit ($\omega(i) > 2000$ ml for both cells). We therefore ignored this effect and replaced Eq. (I.9) by Eq. (I.8) in our analysis.

Computing the excess power according to Eq. (I.11) with all calibration constants as above, we obtain the result shown in Fig. 9. Note that the points for the cell 2 (D_2O) lie slightly above those for cell 1 (H_2O) that are close to zero. However, the (unknown) systematic error due to the contact resistances mentioned above is of the same magnitude (1 W). Furthermore, the excess power is always less than 10% of the input power for cell 2, whereas FP would predict >100% for the size of electrodes we used.

5   Conclusions

We have performed a series of pilot experiments and a concluding experiment to verify the claims made by Fleischmann and Pons of excess heat production during electrolysis of D_2O with Pd electrodes. In our experiment, the 'excess heat' production is of the same size as the systematic error, and therefore insignificant. Unfortunately, we were not able to investigate the systematic errors any further than we did. Further, the maximum excess heat production remains below 10% of the input power, whereas FP predict values an order of magnitude larger. Thus, a firm conclusion is that we have never observed excess powers of the magnitude reported by FP. However, we did not repeat the experiment many times, as FP have suggested.

From the publication by FP [1] we conclude that our measuring set-up is superior to the one used by FP. The possibility for making systematic errors with calorimetry is large, as we have experienced, and we feel that the possibility of making errors with the measurement set-up as presented in [1] is such that the results presented therein must be regarded with some caution.

Acknowledgements

technicians and researchers at the IRI spent much time in analysing our samples and electrolytes. Most of this was done without payment and motivated by enthusiasm, and we are very thankful for the pleasant and inspiring cooperation in these tumultuous months.

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Part II: An attempt to achieve "cold fusion" at high pressure

An investigation into the occurrence of nuclear fusion
in deuterium-loaded palladium

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Abstract

A method is described for achieving high deuterium gas pressures (6 kbar) in small capsules. The method is shown to work successfully.

Pd samples of varying pre-treatment were subjected to these high D_2 pressures, and high loading factors n for the PdD_n system were achieved. The samples were put in non-equilibrium by modulating pressure and temperature. Nevertheless, no neutrons were detected above the background level. The effect claimed by Fleischmann and Pons [1] was not observed.

1   Introduction

The recent announcement by Fleischmann and Pons (FP) [1] and Jones (J) [2] that nuclear fusion might occur in metals loaded with deuterium by means of electrolysis has led to world-wide efforts to duplicate their results. Speculations about more favourable conditions under which to conduct the experiments than the ones used by the FP and J groups have led to such experiments as the one conducted at Frascati by Scaramuzzi, that involved loading Ti with D by application of D_2(g) at $5 \cdot 10^6$ Pa pressure, at liquid nitrogen temperatures (77K) [3]. The Frascati group claimed to measure high neutron yields during loading and unloading of the sample, suggesting that the fusion, if indeed that is the source of the neutrons, is typically a non-equilibrium process.

2 Design of the experiment

By studying the phase diagram of H in Pd (Fig. 10), which does not differ much from that of D in Pd, it becomes clear that the loading factor $n = n_H/n_{Pd}$ can reach high values at low temperatures without the need of a high pressure ($n \geq 0.75$ at $T \leq 20$ °C and $p = 5 \cdot 10^6$ Pa) [4]. However, operation of this experiment at low temperatures has two distinct disadvantages: during loading and unloading the metal hydride repeatedly passes through the two-phase region, leading to internal stresses and eventually to complete destruction of the metal lattice structure. Furthermore, the diffusion coefficient of H or D in palladium is, classically,

$$D^{H/D} = D_0^{H/D} \exp\left[\frac{-E_a^{H/D}}{k_B T}\right], \tag{II.1}$$

Fig. 10. *Pd-H phase diagram (cf. Fig. 1) including data obtained at high pressure [7]. The isotherms of the Pd-D system differ only slightly from these.*

where E_a is the diffusion activation energy, $E_a^H \approx (0.232 \pm 0.004)$ meV, $E_a^D \approx (0.211 \pm 0.005)$ meV , $D_0^H \approx (3.4 \pm 0.8) \cdot 10^{-3}$ cm²s⁻¹ and $D_0^D \approx (2.1 \pm 0.8) \cdot 10^{-3}$ cm²s⁻¹ [5]. Equation (II.1) indicates that the diffusion coefficient of hydrogen in the metal drops significantly with decreasing temperature, thus slowing the process.

Because the mechanism of the 'fusion' process is as yet unknown, it may well be that the two 'disadvantages' mentioned above are, in fact, essential to its occurrence. It has been suggested that in Pd with many defects the D prefers to cluster near the defects in molecular form (D_2). This would lower the density of interstitial D in the metal lattice, which is probably detrimental to the occurrence of fusion, as it is known that no fusion takes place in D_2-gas.

To shed some light on this issue, we designed two experiments, one with maximum lattice homogeneity, and one with a large number of lattice defects. We annealed the Pd at temperatures close to its melting point (1552 °C), thus hoping to improve lattice homogeneity and to remove some impurities. Subsequently one of the cylindrical samples was shortened axially by 10% in order to create a high concentration of lattice dislocations. Both Pd samples were then loaded with D at temperatures above 298 °C, the critical temperature of PdH, thus
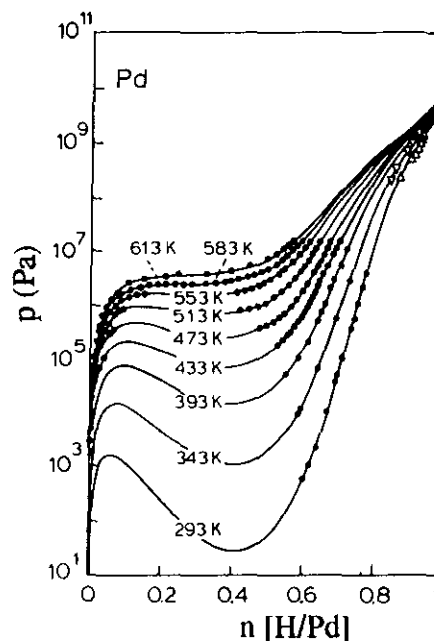
avoiding lattice destruction during loading of the Pd samples. To achieve a loading factor n around 0.95, we applied D_2 pressures of up to $0.6 \cdot 10^9$ Pa (Fig. 2 gives experimental data). We monitored the neutron production near the sample.

The high D_2 pressure was produced in a gold capsule containing the Pd sample, D_2O and Ta powder (a sketch is shown in Fig. 11). In this system, the following reactions will occur at sufficiently high temperatures:
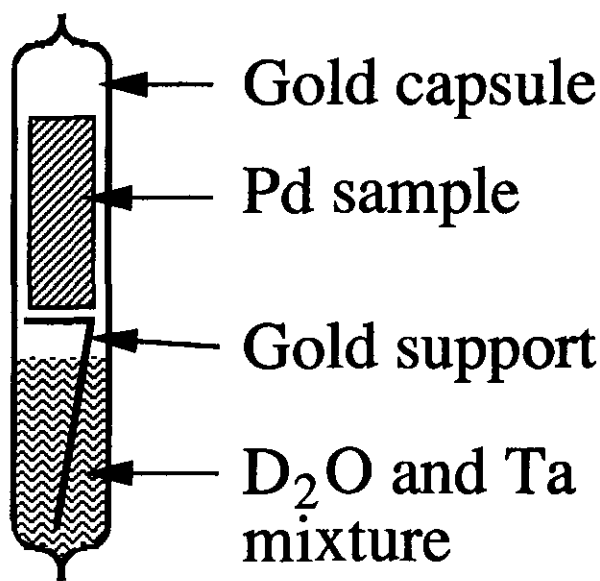
$$D_2O \leftrightarrow D_2 + \tfrac{1}{2}O_2 \tag{II.2}$$

$$2Ta(s) + \tfrac{5}{2}O_2 \leftrightarrow Ta_2O_5 \tag{II.3}$$

$$Pd + \tfrac{n}{2}D_2 \leftrightarrow PdD_n \tag{II.4}$$

Fig. 11. *Schematic of the capsule containing the Pd sample. The gold tube is welded shut at both ends.*

The equilibrium of reaction (II.2) will be strongly balanced towards the left, but as reaction (II.3) removes the oxigen almost completely (at room temperature the reaction constant $Log_{10}Kf = 344.94$ [6]), reaction (II.2) will be pulled towards the right, so that large D_2 pressures can be built up. Provided enough D_2O and Ta powder is present, the final D_2 pressure will be equal to the externally imposed pressure (6 kbar Ar). The outward diffusion of D through the Au cylinder is known to be small at room temperature.

The neutron counting equipment consisted of a ^3He counter tube attached to a high voltage supply and an amplifier connected to a multichannel analyser. The counter efficiency has been determined as $(9 \pm 1) \cdot 10^{-4}$ cts/neutron (2.5 MeV) at a sample to counting tube distance of 0.1 m. FP report a fusion rate of 10^{-19} fusions / D pair / s [1], while J reports 10^{-23} fusions / D pair / s [2]. Assuming a loading factor of n = 0.9, and that every other fusion yields a neutron (i.e. a 50% branching ratio is assumed between the

two standard D-D fusion reactions [1,2]) we can compute the expected count rate for the two cases:

$$R_J = m_{Pd} \cdot 1.1 \cdot 10^{-5} \text{ cts/s}$$

$$R_{FP} = m_{Pd} \cdot 1.1 \cdot 10^{-1} \text{ cts/s},$$

where m_{Pd} is the mass of the Pd sample in g. The background count rate has been measured at the laboratory over several days, and was found to be to be $3.9 \cdot 10^{-2}$ cts/s, so that, taking m_{Pd} = 2 g, the FP effect should be clearly visible (a factor five above background), while the J effect lies below our detection limits. A severe drawback of the set-up is that only one neutron counter was available such that the background could not be monitored during the experiment itself.

In the following sections, two experiments are discussed. The first is a pilot experiment that served to pave the way for the second one. The first experiment involved only one Pd sample. The second experiment was carried out with two samples, as described above.

3   Experimental results

3.1   Experiment 1

The Pd sample (Table II.1) was annealed at 1500 K under a nitrogen atmosphere. It was then placed in a gold capsule (inner diameter, i.d. = 5.4 mm, outer diameter, o.d. = 5.8 mm) containing some Ta powder (grain size < 40 μm), D_2O and a small gold support for the Pd. Some additional space was left to allow for expansion of the water at elevated temperatures. The capsule was welded shut while being cooled to prevent any heavy water from evaporating. It was then tested in vacuum for leaks. None were found.

Table II.1   Numerical data for experiment 1

Pd Mass	Pd Length	Pd Diameter	Ta Mass	D_2O Mass
1.8434 g	12.13 mm	4.03 mm	1.323 g	0.190 g

The capsule was then placed in a cold-seal, externally heated pressure vessel (l = 204.9 mm, o.d. = 36.2 mm, i.d. = 6.52 mm; Boyd, England), using Ar as the confining medium. The neutron counter was placed at 7 cm (centre of sample to centre of counting tube) distance from the sample. The pressure was raised to 3 kbar. One hour later the temperature was raised to 600 °C to oxidize the Ta and jump over the two-phase region in the PdH diagram. After an hour, the

experiment was left to cool gradually, and after another hour the pressure was brought to 6 kbar. After one more hour the system was again brought to 600 °C at 3 kbar and left overnight to oxidize any remaining Ta. The system was then brought to 6 kbar at room temperature and left for 4 days. The neutron count rate remained at background level during the entire experiment (Fig. 12).
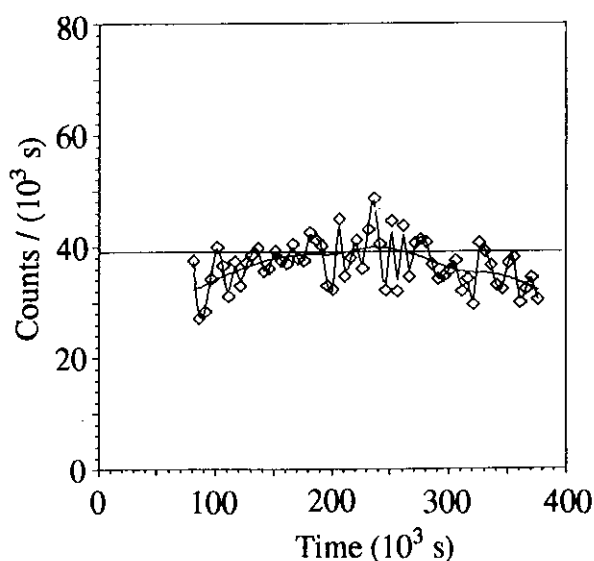

Fig. 12. *Neutron counts versus time for experiment 1. Each dot is an average over 5000 s. The curves are short- and long-term averages. The horizontal line is the background level.*

"Post mortem" analysis revealed the following. The weight of the capsule was reduced by 5.2 mg. Assuming that this was due to diffusion of D_2 through the Au capsule, 1.3 mmol D_2 was lost. After perforating the gold capsule in vacuum, 2 mg D_2O was captured in a cold trap at LN temperature. 27 ml gas of 1 bar at room temperature was captured in a vacuum line and analysed with a mass spectrometer. Most of it had mass 4 (D_2), some of it 3 (HD), and a very small part had mass 2 (H_2). The capsule was then taken apart. At the sample-capsule interface, the capsule had formed an alloy with Pd. The Ta oxide came in two colours: white and grey. The opened capsule was put in a dry oven at 130 °C for one hour, during which any remaining D_2O should have disappeared. The Pd was put in vacuum and the escaping gas was caught. 125 ml of gas at 1 atm. was collected. This would correspond to a filling factor of 0.6 as a lower limit. However, some D_2 will have escaped while the capsule was in the dry oven. An estimate of the actual filling factor, made by adding all (unaccurately known) amounts of D_2 lost in the various stages of the "post mortem" analysis described above, gives 0.8. The Ta oxide was analysed using X-ray diffraction techniques. It was found to consist for the greater part of Ta_2O_5 (white) and somewhat less of TaO (grey).

3.2 Experiment 2

The second experiment improved on the first one by pre-loading the Pd with D with the installation the FOM Institute had developed for this purpose. The advantage of this procedure is that the filling factor of the PdD_n system already is n = 0.6 at the onset of the experiment. Two Pd samples (2A and 2B) were used (see Table II.2 below). They were annealed at 1500 K for 2 hrs and gradually cooled to room temperature. Sample 2B was shortened axially by 10% in an Instron servo-controlled testing machine. This procedure induced a large amount of dislocations, which, according to speculation, might enhance the occurrence of so-called 'crack-induced fusion'.

Table II.2	Pd samples of experiment 2			
Sample	Mass	Length	Diameter	Deformed
2A	1.4226 g	9.45 mm	4.02 mm	no
2B	1.4010 g	8.28 mm	4.28 mm	yes

Both samples were pre-loaded with D_2 gas at 80 bars pressure and at 425 °C at the FOM Institute. The samples were then put in small containers with D_2O, cooled to liquid Nitrogen temperature and transported to the HPT Laboratory, where they were put in gold capsules with Ta powder and D_2O (Table II.3). The capsules were then welded shut.

Table II.3	Contents of capsules of experiment 2		
Capsule	Pd sample	Ta powder	D_2O
2A	1.4226 g	1.0319 g	0.2267 g
2B	1.4010 g	1.0295 g	0.2211 g

Pilot experiments with Ta powder were performed in order to establish the time needed for complete oxidation. A Temperature-Gravity Analysis showed that Ta oxidizes explosively in an oxygen atmosphere (1 bar) at 550 °C, while only reacting slowly below that temperature. Experiments at 3 kbar showed that Ta oxidizes fully at 600 °C in an H_2O environment in less than 2 hrs; does not oxidize at all at 300 °C in 4 hrs, and oxidizes for the best part at 500 °C for 1 hr. We chose the latter circumstance for our experiment, since we did not want to have our

capsule at high temperatures for very long, as the diffusion of D_2 through Au increases very strongly with temperature.

We measured the neutron background at the laboratory for 9 days (a spectrum is shown in Fig. 13). We observed a slow (timescale 1 day), small variation in the background level (maximum 0.003 cts/s). The background was established at (0.039 ± 0.002) cts/s.

Capsule 2A was put in the pressure vessel and the pressure was raised to 6 kbar. After an hour the pressure was reduced to 3 kbar and the capsule was heated to 500 °C and left for an hour in order to oxidize the Ta powder. The sample was cooled to room temperature using pressurized air and was left at 6 kbar for 3 days. No neutrons were detected above background level (Fig. 14).
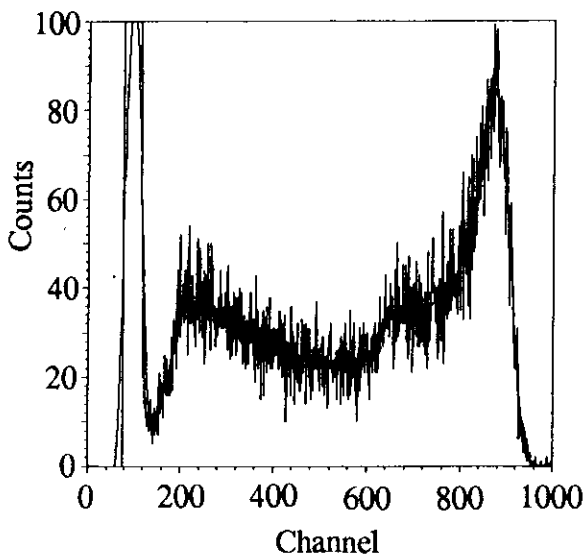
Fig. 13.   Spectrum of the neutron background taken over a period of 9 days. The horizontal axis is not calibrated; however, the three peaks at $\frac{1}{4}$ E, $\frac{3}{4}$ E and E (i.e. at channel 215, 645 and 860), characteristic of a neutron spectrum, can be seen.
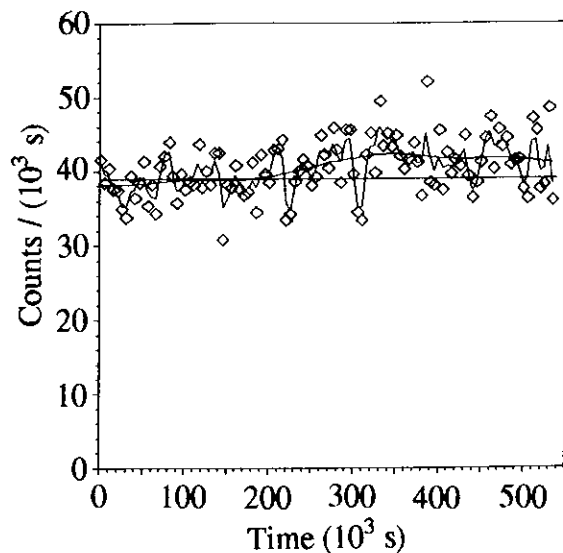
Fig. 14.   Neutron counts as a function of time for experiment 2A. Each dot is an average over 5000 s. The curves are short- and long-term averages. The horizontal line is the background level.

To create possibly beneficial non-equilibrium conditions, the temperature was modulated between room temperature and 50 °C higher with a period of 2 hrs for 22 hrs. A correlation analysis between the temperature and the neutron count was performed (Fig. 15). No correlation was found. The following day the experiment was terminated.

The capsule looked swollen, indicating high internal D_2 pressure, but it did not have any leaks. The capsule was then thrown in liquid Nitrogen with the neutron counter at approximately 15 cm. No excess neutrons were detected.

A similar procedure was applied to capsule 2B, except that instead of a temperature modulation we tried a pressure modulation after leaving it at 6 kbars for three days first. The pressure was alternated between 3 and 6 kbar with a period of 1 hr for $3\frac{1}{2}$ hrs. No excess neutrons were detected. After this we again applied the temperature modulation for $1\frac{1}{2}$ days, but no excess neutrons were detected.

Upon termination of the experiment the capsule leaked. From the appearance of the Ta and Ta-oxide and the presence of a small amount of fluid near the top end of the capsule we deduced, however, that the leak must have sprung during depressurization near the end of the experiment.

Both capsules were opened, and the Pd samples were stored in liquid Nitrogen and sent to the IRI (Delft) for analysis. Unfortunately, the capsules were exposed to room temperature for a few hours before analysis. This will have reduced the deuterium content of the Pd samples, especially with sample 2B (the leaking capsule). Nevertheless, IRI analysis revealed n = 0.6 (2A), and n = 0.8 (2B). The actual value of n during the experiment must necessarily have been higher.
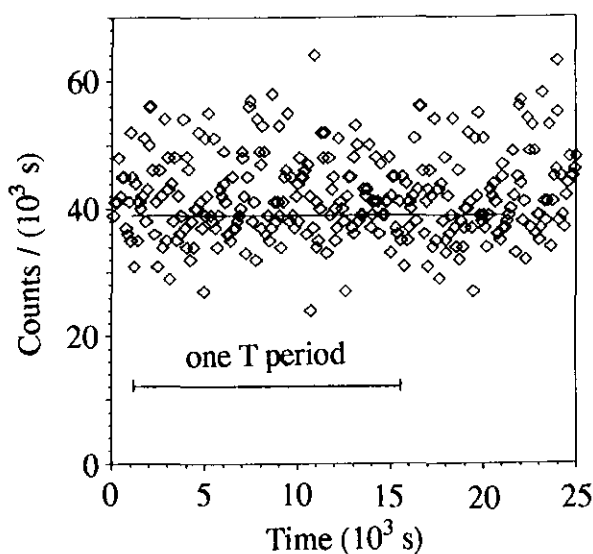

Fig. 15. *Neutron counting data taken over a period of 22 hours. The data have been coherently summed to display any possible correlation with the temperature variation having a period of 2 hours. No correlation is visible.*

4   Conclusions

We have succeeded in achieving high deuterium gas pressures in gold capsules containing heavy water and Ta powder, by means of heating and pressurizing the capsules at 6 kbar. This high deuterium pressure was used to obtain a high loading factor n of the PdD_n system, by including a Pd sample in the capsule. The method has been shown to be successful by verification of n through analysis at the IRI Institute: n > 0.8. This is close to the highest value for n reported in literature (n = 0.9) [7], which was achieved by a far more complex method and pressures more than twice as high as ours.

The pressurized capsules, containing Pd samples that were either annealed or that had a large number of deliberately induced dislocations, were monitored for neutron production. The samples were brought into non-equilibrium by applying temperature modulation or pressure modulation. Upon termination of the experiments, the samples were cooled to LN temperature. During the entire experiment the neutron flux level did not rise above the background level within measuring accuracy.

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