EXCESS HEAT AND NUCLEAR PRODUCT MEASUREMENTS IN COLD FUSION ELECTROCHEMICAL CELLS

D. Gozzi, R. Caputo, P. Luigi Cignini, M. Tomellini
Dipartimento di Chimica, Università La Sapienza, P.le Aldo Moro 5, 00185 Roma, Italy

G. Gigli, G. Balducci
Dipartimento di Chimica, Università La Sapienza, P.le Aldo Moro 5, 00185 Roma, Italy

E. Cisbani, S. Frullani, F. Garibaldi, M. Jodice, G. Maria Urciuoli
Laboratorio di Fisica, Istituto Superiore di Sanità, V.le Regina Margherita 299, 00161 Roma

Abstract

We present the results of a new experiment with our multicell set-up implemented with mass spectrometric measurements of $^4$He and a highly improved neutron detector. The excess heat measured is in line with our previous results as well as with other laboratories while no neutrons, and a tritium excess lower than expected from power excess were found. $^4$He has been measured in the electrolysis gases and a tentative correlation of $^4$He with excess power is presented and discussed.

Introduction

Since 1989, in various countries around the world, continuous efforts have been done to investigate the nature of the excess heat found in electrochemical experiments of loading palladium or palladium alloys by deuterium. Five years about of such as experiments carried out by several groups, by using different techniques and procedures indicate that the heat power excess findings, up to 3.7 kW/cm$^3$ of Pd (1), cannot be attributed to artifacts and their magnitude appears well beyond the power that any expected chemical process could release. If adequate protocols are used, heat generation is found and quite definite progress

1To whom any correspondence should be addressed
2CNR-Centro di Termodinamica Chimica alle Alte Temperature, c/o Dipartimento di Chimica, Università La Sapienza
3Dipartimento di Scienze e Tecnologie Chimiche, Università Tor Vergata, Via della Ricerca Scientifica, 00133 Roma
4National Institute for Nuclear Physics (INFN) sez. Sanità, V.le Regina Margherita 299, 00161 Roma
has been made towards its reproducibility though it is still difficult to adequately control its onset, duration and magnitude. Because these features are the primary conditions for developing any type of technologically exploitable energy-producing device, efforts for improving them are in progress, especially by private companies, mostly in Japan.

On the side of nuclear ashes recovery, the overall picture is more intriguing. At present time one thing is very well confirmed: the generation rate of neutrons and tritium nuclei, coming from the $d,d$ reaction channels, thought as occurring in plasma physics, are of several order of magnitude lower, if compared with the rate values expected from heat power excesses measured by calorimetry. Therefore, in condensed matter, other nuclear byproducts of $d,d$ reaction have to be invoked and searched. In this two-body reaction, only another channel can exist: the $^4$He channel. Since the beginning, various measurements (2-8) to detect $^4$He both in Pd cathodes and in the gas phase escaping from the electrochemical cells were reported but only a few of them are accounted for in detail. Up to now only one electrochemical cells experiment has been reported (3) where evidence is given of heat excess roughly correlated with $^4$He measured in the gas phase. The air contamination which could have possibly occurred in this experiment was later discussed (5). Gas loading experiments in a high vacuum assembly have clearly shown the release of $^4$He when deuterium is confined in Pd between blocking interfaces (6).

From the theoretical point of view, there are at least two great problems to solve for explaining this experimental scenario: i. Coulomb barrier for $d,d$ reaction between low energy nuclei; ii. the energy release to Pd lattice of the $\alpha$-particle produced. In terms of plasma physics, for both these problems there is not a solution. On the other hand these problems have been attacked with promising results by some theories (9-12). Their main feature is the attempt to overcome the schemes of the high energy physics believed to be not fully apt to treat a different physical situation such as that of the condensed matter.

All this is a bird-view emerging from four International Conferences (13-16), specialized International Meetings (17-18) and several hundreds of publications on Journals.

Starting from 1989, our group, where competences of physical chemistry and nuclear physics are present, is with continuity involved in making multicell experiments providing calorimetric and nuclear (neutrons, tritium, $^4$He, gammas) measurements as well as a little bit of Materials Science applied to Pd cathodes preparation (19-27). Scope of the present paper is to show a part of the results obtained in the last multicell experiment in which the feature of the quantitative measurement of $^4$He was added.

Experimental Overview

The basic idea in designing our experimental set-up was to have a multicell system, up to ten equal cells, in which the unique difference among them was in the cathode in terms of material or geometry or preparation. One or more cells can be blank cells having the cathode made of a material not D (H) absorbing such as Pt or Au or made of Pd but in a D free electrolyte. All the cells are connected in series and electrolysis is carried out in galvanostatic mode (each cell can be excluded or inserted at any time in the electrical series circuit by a home-
made device controlled in manual or by computer mode). This allows the rate of all the electrochemical processes be the same in each cell. This condition produces a certain number of important facts related to the calorimetry; as an example, the flow-rate of the electrolysis products, D₂ (g) and O₂ (g), is, according to the Faraday's law, equal in each cell⁵ so that the heat transported by the escaping gases and the heat necessary to saturate the gases themselves by D₂O (H₂O) are also the same in each cell provided the temperature of the solution be the same.

Because each cell is a non-adiabatic calorimeter, it is important that the way the heat is exchanged with the surroundings is the same for all the cells. As expected, this has to occur mostly through the conductive path localized in the cell glass wall between the electrolyte solution and the thermostated stream of circulating water. This is obtained by positioning all the cells symmetrically in a torus-shaped bath thermostated by circulating water kept at constant temperature (generally 21.0 ± 0.1 °C) by a high quality thermostat. The room temperature is maintained close to this value.

The torus (50 cm outer diameter and 30 cm innermost diameter) is contained in a large neutron counter designed by us and manufactured by Jomar-Canberra, Los Alamos (see below).

To easier understand what is monitored, what is done in each cell and how the signal are processed, we report in Fig. 1 the complete flow-chart (24).

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⁵To be correct this is exactly true when the rate of D (H) absorption by the cathode is zero. For practical purposes, this condition is fulfilled quite soon after the starting of electrolysis.
All the cells are treated according to this flow chart. As it is shown in figure 2, our cells are open-type cells with external recombination. The external recombinator joined to the D$_2$ (H$_2$) separator is an efficient D$_2$ (H$_2$) cutting system (see below).

$^4$He measurement by a magnetic type mass spectrometer (28) is not an on-line measurement and the gas line is sampled discontinuously by filling a 500 ml stainless steel (SS) cylinder. At sampling stage, as it will be shown later on, the gas composition is given by N$_2$ with D$_2$ (H$_2$), O$_2$ and D$_2$O (H$_2$O) traces and $^4$He if any. At certain stage of the experiment $^{20}$Ne measurements have been initiated as a marker of a supposed air contamination.

In the followings, we shall describe, except for the $^4$He measurement procedure reported elsewhere (28), the single parts of the experimental set-up as well as the adopted procedures, making use of what was already reported (24-26) while describing in details the new features and the reliability of the various methods adopted.

**Electrochemical Cells and Calorimetry**

**i. Electrochemical cell.**

The present most recent version of the electrochemical cell is reported in Fig. 2. This cell was modified with respect to the previous version (26) essentially to make it impervious to the air contamination in view of $^4$He measurements. In fact, particular care has been reserved to all the feedthroughs in the cap in making them tight by high precision machining of the crossing holes as well as in selecting the feedthrough material. Nylon 66 or SS tubes were adopted for the lines because, as we tested (28), they are not $^4$He permeable. Connections in the lines were done by Swagelock fittings and where this was not possible, as in the case of SS-Pyrex joints, we made them by soldering SS tube and Pyrex by epoxy resin adhesives (of the types used in high vacuum technology). To carry $^4$He up to the sampling cylinder, due to the deuterium cutting system, we have to use a stream of N$_2$ coming from a LN$_2$ tank. This ensures a practical null background of $^4$He (28).

The cell geometry (inner diameter 22 mm x 245 mm height) was designed to maximize the heat transfer in the radial direction by taking also into account the combined effect of the carrier and electrolysis gases bubbling which jointly allow the thermal gradient to be localized on the plane orthogonal to the z-axis of the cell. The effective volume of the cell to be filled with the electrolyte solution is about 53 ml. Small deviations from this value may exist from cell to cell if the cathodes are different in size.

Three K-type thermocouples are present in the cell to measure the temperature of the cathode, solution and just outside the cell in a massive copper ring immersed in the thermostated bath. Automatic and computer controlled refilling of D$_2$O (H$_2$O) is operated by the liquid sensor level positioned in the lateral tube.

To ensure a good and permanent coaxial positioning of the electrodes, both the cathode and anode are partially inserted in a properly machined Teflon piece which also acts as N$_2$ scrubber in its bottom part.

The anode is made of a 1 mm diameter Pt wire shaped as coil having 12 mm inner diameter and height comparable to that of the cathode.
The electrolyte solution is 0.2 M solution of LiOD in 99.99% D₂O (from ISOTEC, USA) at low tritium content (≈ 1Bq/ml or 60 dpm/ml). The ICPAES (Inductively Coupled Plasma Atomic Emission Spectroscopy) analysis of the starting solution did not detect any alkaline or heavy metal above the detection limit which is generally ≤ 10 ppb.

In Table I are reported some of the features of the cells tested in this experiment. All the Pd cathodes were prepared starting from Johnson & Matthey (UK) rods.

Table I. Details of the electrochemical cells used in this experiment

<table>
<thead>
<tr>
<th># cell</th>
<th>cathode size [mm x mm]</th>
<th>Treatment</th>
<th>Gas line material</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pt 1 x 23</td>
<td>as received</td>
<td>SS</td>
<td>blank</td>
</tr>
<tr>
<td>2</td>
<td>Pd 2 x 25</td>
<td>as received</td>
<td>Nylon</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Au/Pd 6 x 23</td>
<td>HV at mp of Au</td>
<td>SS</td>
<td>D₂ Confinement experiment (32)</td>
</tr>
<tr>
<td>7</td>
<td>Pd 2 x 21</td>
<td>screw dislocated</td>
<td>Nylon</td>
<td>switched on from 675 to 930 hrs</td>
</tr>
<tr>
<td>8</td>
<td>Pd 3 x 22</td>
<td>screw dislocated</td>
<td>Nylon</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Pd 3 x 23</td>
<td>as received</td>
<td>Nylon</td>
<td></td>
</tr>
</tbody>
</table>
Calorimetry

The calorimetric excess heat measurements are based on the comparison of the actual value of temperature of the solution at a given input power with the calibration curve. The calibration curve is obtained by increasing or decreasing in step-fashion the input power. This can be done either in thermal mode, by the inner heater, or in electrochemical mode by using Au or Pt cathodes exactly in the same conditions in which the experiment is subsequently carried out. A detailed discussion about those procedures has been already reported in literature (25-26), therefore we limit ourselves to give in Table II the calibration curves equations for the cell used in this experiment.

Table II. Calibration curves: \( P_{in} = (a_i \pm \Delta a_i) + (b_i \pm \Delta b_i) \Delta T_i \)

<table>
<thead>
<tr>
<th>Cell/i</th>
<th>( a_i /W )</th>
<th>( \Delta a_i /W )</th>
<th>( b_i /W K^{-1} )</th>
<th>( \Delta b_i /W K^{-1} )</th>
<th>( r )</th>
<th>( P_{exc,i}^{\text{max}} /W )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.7</td>
<td>0.5</td>
<td>7.0</td>
<td>0.1</td>
<td>0.9983</td>
<td>1.7±0.7</td>
</tr>
<tr>
<td>2</td>
<td>0.3</td>
<td>0.7</td>
<td>5.8</td>
<td>0.1</td>
<td>0.9985</td>
<td>1.2±0.8</td>
</tr>
<tr>
<td>4</td>
<td>0.06</td>
<td>0.60</td>
<td>5.5</td>
<td>0.1</td>
<td>0.9979</td>
<td>0.9±0.7</td>
</tr>
<tr>
<td>7</td>
<td>0.5</td>
<td>0.3</td>
<td>5.06</td>
<td>0.07</td>
<td>0.9993</td>
<td>1.3±0.3</td>
</tr>
<tr>
<td>8</td>
<td>-0.6</td>
<td>0.4</td>
<td>5.21</td>
<td>0.09</td>
<td>0.9991</td>
<td>0.2±0.4</td>
</tr>
<tr>
<td>10</td>
<td>-0.5</td>
<td>0.9</td>
<td>6.3</td>
<td>0.2</td>
<td>0.9968</td>
<td>0.4±0.9</td>
</tr>
</tbody>
</table>

All the curves are practically straight-lines with high correlation factor \( r \) having the general equation form as: \( P_{in} = (a_i \pm \Delta a_i) + (b_i \pm \Delta b_i) \Delta T_i \) where \( \Delta T_i = (T_i - T_s) - (T_{ib} - T_{sb}) \), with \( T_s \) and \( T_{ib} \) respectively, the temperature of the solution and of the thermostated bath just outside the cell and measured in the copper ring. \( T_s \) and \( T_{ib} \) are the respective values of \( T_s \) and \( T_{ib} \) kept at \( P_{in} = 0 \). \( P_{in} \) is the input power equal to \( IxV \) or \( Ix(V - V_{th}) \) depending on whether the cell is powered in thermal or electrochemical mode. \( V_{th} = \Delta H^o/2F \) is the thermoneutral potential being \( \Delta H^o \) the enthalpy of decomposition of D\(_2\)O (H\(_2\)O) and \( F \) the Faraday constant. The adopted value of \( V_{th} \) for D\(_2\)O is 1.5367 V (29). \( V_{in} \) and \( I \) are, respectively, the electrical potential difference at leads read closest to the heating resistor, when in thermal mode, or electrodes, when in electrochemical mode and current measured through the voltage drop at leads of a high precision 100 mΩ resistor. The overall uncertainty in measuring \( P_{in} \) is 0.01%. The heat power excess, \( P_{exc} \), of a given cell \( i \), is given by:

\[
P_{exc,i} = P_{out} - P_{in} = a_i + b_i \Delta T_i - P_{in}
\]

where \( \Delta T_i \) is now the value measured in the experiment. The overall error on \( P_{exc} \) has been evaluated to be less than ±10% (25). The minimum heat power excess detectable is given by \( P_{exc,i}^{\text{min}} \geq (a_i \pm \Delta a_i) + (b_i \pm \Delta b_i) \Delta T_i \), where \( 0.1 < \Delta T_i \leq 0.2 ^\circ \text{C} \), is the minimum temperature change appreciable by the K-type thermocouples used. In Table II, the \( P_{exc,i}^{\text{max}} \) column was calculated assuming \( \Delta T_i = 0.15 ^\circ \text{C} \). Note that due to the definition of \( \Delta T_i \), the systematic error on this quantity is practically zero.

The energy balance of such a calorimeter during a calibration input power step is given by:
\[ P_n = m_i C_i \frac{\partial \Delta T_i}{\partial t} + \pi \frac{dk_{\text{Pyrex}}}{l} \Delta T_i(t) + \frac{k_{\text{rad}}}{\pi \Delta h} \left([T_{\text{sb}} + \Delta T_i(t)]^4 - T_{\text{sb}}^4\right) + \]
\[ + \left( \frac{3I}{4F} + \frac{P}{RT_{\text{t}}} \right) \left[ \frac{p(t)}{P - p(t)} \right] \left[ (C_s - C_i)_{D_2O} \Delta T_i(t) + \Lambda_{\text{vap}} \right] \]

where the four terms on the right side represent, respectively, the rate of enthalpy change of the solution, the rate of heat transfer from solution to the thermostated bath by conduction through the Pyrex wall, the rate of heat transfer by radiation to the thermostated bath and rate of heat transfer from solution to the gases (produced by electrolysis + N_2 carrier) escaping from the cell and saturated with D_2O (H_2O) at the temperature of solution. Consult Appendix A for the meaning of symbols in Eqn. 2. Due to the continuous heat transfer to the thermostated bath, \( \Delta T_i \), contrarily to an adiabatic calorimeter (1), is generally below 15 °C, and therefore also the vapor pressure of D_2O (H_2O) is low with respect to the atmospheric pressure and the term \( \left[ \frac{p(t)}{P - p(t)} \right] = 2 \times 10^{-2} \). The sign of the last contribution to the sum of the right side member of Eqn. 2 depends on the sign of the term \( \left[ (C_s - C_i)_{D_2O} \Delta T_i(t) + \Lambda_{\text{vap}} \right] \) which is always > 0 in the useful working temperature range (it becomes < 0 at \( \Delta T_i(t) = -\frac{\Lambda_{\text{vap}}}{(C_s - C_i)_{D_2O}} > 906.5 \) °C !!) whereas the overall magnitude can be evaluated close to = 4.5 mW for I < 1A and \( f_{\text{t}} = 5.4 \times 10^{-7} \) m^3s^{-1} at stp (see below).

The radiative term \( k_{\text{rad}} \left([T_{\text{sb}} + \Delta T_i(t)]^4 - T_{\text{sb}}^4\right) \), for the same above considerations on \( \Delta T_i \), is evaluated ranging around 3 mW and, therefore, for practical purposes Eqn. 2 can be written as

\[ P_n = m_i C_i \frac{\partial \Delta T_i}{\partial t} + \pi \frac{dk_{\text{Pyrex}}}{l} \Delta T_i(t) \]  

It is important to point out that in the case of determination of \( P_{exc} \), Eqn. 2 might be put in the form:

\[ P_{exc,i}(t) = m_i C_i \frac{\partial \Delta T_i}{\partial t} + \pi \frac{dk_{\text{Pyrex}}}{l} \Delta T_i(t) + \Phi[\Delta T_i(t)] - P_{n,i}(t) \]

where, in the term \( \Phi[\Delta T_i(t)] \) are now considered the sum of both the terms previously neglected. It is easy to verify that the elimination of \( \Phi[\Delta T_i(t)] > 0 \) from Eqn. 4 always produces an underestimate of \( P_{exc} \).

The integration of Eqn. 3, in the case of a calibration step of input power, gives:
\[ \Delta T_i = \frac{\tau}{\zeta} \left( 1 - e^{-\frac{1}{\tau}} \right) = \Delta T_{i,\text{initial}} \left( 1 - e^{-\frac{1}{\tau}} \right) \]

\[ \tau = \left( \frac{\pi d h k_{\text{pre}}}{l \zeta} \right)^{-1} ; \quad \zeta = m_i C_i ; \quad \Delta T_{i,\text{initial}} = \left( \frac{\pi d h k_{\text{pre}}}{l} \right)^{-1} P_m \]

where the term \( \left( \frac{\pi d h k_{\text{pre}}}{l} \right)^{-1} \) is the slope of the calibration curve which corresponds to the \( (b_i)^{-1} \) parameters shown in Table II. The theoretical time constant value is \( \tau = \frac{\zeta}{b_i} = \frac{\rho b_i V^0 C_i}{b_i M} = \frac{280}{b_i} \) s. Higher values (350-400 s) of \( \tau \) are experimentally found due to the fact that the \( \zeta \) term should be more correctly written as \( \zeta = m_i C_i + \sum m_i C_i \) where the summation runs on all the masses present in the cell. If a set of points is obtained in stationary condition of \( \Delta T_i \) associated each time to a different \( P_{\text{in}} \) value, provided \( h \) is kept constant by a level sensor, this set has to be, within the experimental errors, on a straight-line of slope \( \left( \frac{\pi d h k_{\text{pre}}}{l} \right)^{-1} \) since this value depends only on constant quantities. This is just what we in fact obtained, as shown in Table II. To check the validity of the treatment above, one can obtain \( k_{\text{pre}} \) from the slope of the calibration curve. The averaged value obtained is 0.9 ± 0.1 Wm⁻¹K⁻¹ which is in agreement with the value reported in literature (30) (see Appendix B).

**Deuterium cutting system**

It is composed by two parts connected in series by SS (inner diam. 1.5 mm) or Nylon66 (inner diam. 3 mm) tubing: i. catalytic recombinator and ii. Pd sponge trap. This operation allows to measure tritium in the electrolysis gas phase (see below) and eliminate \( D_2 \) from the gas stream before sampling for \( ^4 \)He analysis.

i. **Catalytic recombinators.**

They are described elsewhere (25). Their yield \( \eta \) is calculated by the following equation:

\[ \eta = \frac{\nu_{\text{recomb}}}{\nu_{\text{in}} - \nu_{\text{cond}} - \Delta \nu} = \frac{\nu_{\text{pre}} - f_{\text{cond}} \Delta \nu}{2 F \int \Delta \nu \text{d}t} \]

measuring the recombined volume of \( D_2O \) in the time interval \( \Delta \nu \). The correction for the condensation of \( D_2O \) contained in the gas stream was measured to be 3.75x10⁻⁶ cm³s⁻¹. The recombination yield value averaged on 10 recombinators is about 92%.

The partial pressure values of \( D_2 \) at the recombinator inlet and outlet are given by the equations:
\[
P_{D_2}^w = \frac{I}{P} \left( \frac{2F}{RT_c} \right) + \frac{3I}{4F} P; \quad P_{D_2}^{\text{eq}} = \frac{I}{P} \left( \frac{2F}{RT_c} \right) + \frac{3I}{4F} (1 - \eta) P 
\]

Supposing, for instance, \( I = 1 \text{A} \), \( \eta = 0.9 \) and using data in Appendix B. \( P_{D_2}^w \) and \( P_{D_2}^{\text{eq}} \) are, respectively, equal to \( 1.74 \times 10^{-1} \text{P} \) and \( 2.28 \times 10^{-2} \text{P} \). This last value is the \( D_2 \) partial pressure of the gas stream entering in the Pd sponge trap.

### ii. Pd sponge trap

Two equal traps, working alternatively and continuously fluxed under \( N_2 \) carrier, when in regeneration, are made of a SS cylinder with an inner coaxial SS tube. The path of the gas mixture inside the trap is such to have the largest contact surface area with the Pd sponge. In each trap are contained 150 g about of Pd sponge from Johnson & Matthey (UK).

If we suppose the absorption reaction

\[
Pd(s) + \frac{y}{2} D_2(g) = PdD_y(s)
\]

completely shifted on the right side, we can define the nominal capacity of the trap as \( C_{\text{nom}} = \frac{y \nu_{PD}}{2 M_{PD}} \), therefore, the residual capacity of the trap with respect to the initial capacity, as a function of \( D_2 \) consumed, is given by:

\[
C_r = 1 - \frac{1 - \eta}{\nu_{\text{nom}}} \nu_{\text{tot}}
\]

It is easy to see that to exhaust a Pd trap, in the case of \( \eta = 0 \), would be sufficient the electrolysis of just 8.5 cm\(^3\) of \( D_2 \). Because in our case \( \eta = 0.90 \), to exhaust completely the trap it would be necessary to make electrolysis of a \( D_2 \) quantity ten times higher.

The minimum partial pressure of \( D_2 \) in the gas stream at outlet of the Pd trap should be equal to the activity of \( D_2(g) \) in the gas phase in thermodynamic equilibrium with the condensed phase at a certain activity of D according to reaction 8. This value can be calculated by the following equation (31):

\[
\ln a_{D_2} = \left[ -\frac{\Delta H_{ab}(y)}{RT_c} \right] + 2 \ln \left( \frac{y}{1 - y} \right) + \frac{\Delta S^{0}_{ab}}{R}
\]

As it is reported elsewhere (32), the background pressure of \( D_2 \) at the outlet of the Pd trap, measured by mass spectrometry, has been found to be \( 5 \times 10^{-10} \text{ atm} \) which, by Eqn. 10 corresponds, to \( y = 0.2 \). Therefore, the overall cutting factor of \( D_2 \), present in the \( N_2 \) carrier at the outlet of the electrolysis cell, is \( 10^8 \) about. This remarkable result joined to the high resolution power of the mass spectrometer allows to be very confident on the quantitative determinations both of \( ^4 \text{He} \) and \( D_2 \).
Measurements of Nuclear Byproducts

1. Tritium.

To prevent any air contamination, contrarily to the past, we did not make tritium tests in the electrolytic solutions of the cells but only in D2O produced by the catalytic recombinators. The experimental procedure adopted to measure tritium was described elsewhere (24) as well as the calculation to evaluate the tritium electrolytic enrichment in the solution. In this experiment, because the tritium measurement is done on the recombined gases and a gas carrier is present in addition to the electrolysis gases, to evaluate correctly the effects of the electrolysis on the tritium concentration in the gas stream it is necessary to modify the mathematical treatment we utilized in the past.

Considerations based on the mass balance of tritium in our cells lead to the following differential equation:

\[
\frac{dn}{dt} = n_{D_2O} \left[ x_f f_{D_2O} \frac{-I}{2F\alpha_T} - x - \frac{p}{\alpha_v (P - p)} f_{D_2O} - x \frac{dn_{D_2O}}{dt} \right]
\]

(11)

As we stated before, in the previous section, the volume of electrolyte has to be constant, therefore, the term \( \frac{dn_{D_2O}}{dt} = 0 \), and so the D2O feed, must be such as to compensate D2O consumed by the electrolysis and D2O evaporated in the gas stream escaping from the cell. If, as it normally occurs, the molar fraction of DTO in the D2O feed is the same as in the D2O initially present in the electrolytic solution, the integration of eqn. 11 gives:

\[
q = q_{lim} - \left( q_{lim} - \frac{1}{\alpha_T} \right) \frac{\nu_{comp}(I, t)}{V^*}
\]

(12)

where the quantity \( q = x_i - x_i^o \) represents the expected change, due only to the electrolysis, of tritium atomic fraction in the gas phase with respect to the initial atomic fraction of tritium in the electrolyte. In eqn. 12 the terms \( q_{lim} \) and \( V^* \) are, respectively, obtained by the equations below:

\[
q_{lim} = \frac{1 + \left( \frac{3}{2} + \frac{2FPf_{x_i}}{RT, I} \right) \left( \frac{p}{P - p} \right)}{1 + \frac{\alpha_T}{\alpha_v} \left( \frac{3}{2} + \frac{2FPf_{x_i}}{RT, I} \right) \left( \frac{p}{P - p} \right)}
\]

(13); \( V^* = \frac{\alpha_T V^o}{1 + \frac{\alpha_T}{\alpha_v} \left( \frac{3}{2} + \frac{2FPf_{x_i}}{RT, I} \right) \left( \frac{p}{P - p} \right)} \)

(14)

In Fig. 3 is reported the \( q_{lim} \) surface in the plane \( V^*, \alpha_T \). Combining eqns. 13 and 14, it is easy to show that only the values of \( V^* \) satisfying the condition

\[
\left( \frac{V^o}{V^*} - \frac{1}{\alpha_T} \right) \geq \frac{3}{2\alpha_v} \left( \frac{p}{P - p} \right)
\]

can be selected in the above plot. In fact the left side term in the inequality has to be positive being the right side term always a
positive quantity. As it appears in fig. 3, the values of the $q_{\text{lim}} \geq 1$ correspond to $V^*$ and $\alpha_E$ values which are without physical meaning.

At fixed temperature and carrier gas flow-rate, an important difference between eqn. 12 and eqn. 2 of ref. 24 (obtained for the tritium enrichment in the electrolyte) is that, $T_{\text{im}}$ and $V^*$ are also function of the electrolysis current whereas the corresponding terms $\alpha$ and $\beta$ are constant quantities. By inspection of eqns. 12 through 14, the following remarks can be drawn:

\begin{align*}
\text{a) at } v_{\text{con}} \rightarrow 0, & \quad q = \frac{1}{\alpha_E} \\
\text{b) at } v_{\text{con}} \rightarrow \infty, & \quad q = q_{\text{lim}}
\end{align*}

\begin{align*}
f_{H_2} = 0 \Rightarrow \frac{1}{\alpha_E} \left[ \frac{1+\frac{3}{2} \left( \frac{p}{p-p} \right)}{1 \alpha_E + \frac{3}{2} \alpha_Y \left( \frac{p}{p-p} \right)} \right] \equiv \frac{1}{\alpha_E} \alpha_E \equiv \frac{1}{\alpha_E} \\
I = 0 \Rightarrow \frac{\alpha_Y}{\alpha_E} \equiv \frac{1}{\alpha_E}
\end{align*}

(15)

---

Figure 3
Calculated surface of $q_{\text{lim}}$ term in eqn. 12 as function of $V^*$ and electrolytic separation factor between deuterium and tritium on a Pd cathode.
Therefore, the expected $q \text{ vs } \nu_{\text{cons}}$ curve starts from $\frac{1}{\alpha_E}$ and remains, of course, at this value if $I=0$ or tends to 1 in the case of electrolysis without any carrier gas stream, whatever is the I value. Since $\alpha_E$ depends mostly from the nature of the cathode, on Pd $\alpha_E = 1.8$ (24-25), it is expected that the $q$ limits will be in the range from $\frac{1}{2}$ to 1. In this experiment, $f_{N_2} \neq 0$ and kept always constant whereas I was changed and in some cases put off for a certain period of time, as it will be shown in the results section. Therefore, we have to expect that throughout the experiment, if tritium is not generated in the cell by a nuclear reaction, the value of $q$ must be within the range $\frac{1}{\alpha_E} \leq q < 1$. Further aspects will be treated in the discussion section.

\textit{ii. Helium-4}

See in this book the paper by the same authors concerning the quantitative mass spectrometric measurements of $^4\text{He}$.

\textit{iii. Neutrons}

A description of our more recent system for neutron detection was already reported (26). However, for the sake of a better understanding of the results, a cross-section of the detector-cell system assembly is shown in Fig. 4.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{detector-cross-section.png}
\caption{Cross section of the neutron detector assembly. Dashed area is the torus containing the electrochemical cells. Black circles represent the $^3\text{He}$ tubes. Each counting group is constituted by five tubes.}
\end{figure}
Data Acquisition System

Two separate data acquisition systems are now at work [only one in the past (24)] in our experiments both based on the network Macintosh Computer ⇔ IEEE-488&RS-232 Interfaces ⇔ Instruments. They are dedicated the first to the neutron acquisition (see before and ref. 26) and the second to the acquisition and control (24) of all the other devices and sensors of the experimental set-up (mostly through a data logger). The programs running on each of the two systems were home-made both realized on the software LabVIEW 2.1.1 from National Instruments (Austin,TX). All the temperature, voltage, current and other analog signals go to the analog input channels of the data logger (Orion 3531 D, Schlumberger,UK) and logged at fixed scan intervals. Generally the scan interval time is set at 300 s but it can change automatically to 5 s if an alarm occurs on one of the logged channels. The alarm feature is based on a preset threshold. All the channels connected to the cathode and solution thermocouples of each cell as well as the counter channel connected in parallel to the TTL logic OR of the neutron counter are set to generate alarms. The primary file (the program generates also other ancillary files as for example those containing dating and volumes of D₂O refillings of each cell) of every piece of data acquisition is constituted of a matrix of 1000 rows x 60 columns which is build by append mode on both the RAM and removable hardisks. A real time plotting of all the channels is at the hand on the computer screen.

Finally, as already mentioned, since the system of all the cells is positioned inside the neutron detector, a B/W TV camera, connected to a videorecorder, is placed in the center of the torus, and operated both in manual and automatic remote control (by data logger), to have a more direct control of the status of each cell.

Results

Calorimetric and 4He data

All the data that will be presented throughout the text are to be intended as obtained according to the step-wise patterns of the electrolysis current as showed in fig. 5 for all the cells tested.

In the four next figures which follow (figs. 6 to 9), two graphs each are reported which represent the 4He and calorimetric results throughout the experiment for some cells. Each figure shows in the upper part the 4He concentration, given in ppb, compared with the 4He concentration in the blank cell and, in the bottom part, the input power (left scale) and heat power excess (right scale). Heat power excess has been calculated according to eqn. 1 and Table II and the related error has to be considered conservatively equal to ±10% of the value while the error on the input power is, as already mentioned, negligible. Because of the high number of points composing each curve (>10⁴), in order to obtain a better readability, the errors bars are not reported in the bottom graphs. To facilitate a comparison of the energy quantities involved both the scales have the same limits. Furthermore, the lack of heat excess results in some parts of the related curve is due to a conservative choice we adopted in not considering those data which were acquired in experimental conditions not exactly equal to the ones in which the calibration curve had been obtained. The error on 4He concentration

6 Connected to some electrical perturbations induced during the D₂ confinement experiment on cell #4
has been estimated equal to ± 13% of the value (28) Cells #1 and #7 did not show any excess of heat power within the experimental error. For cell #1, this is as expected because it is the blank cell. Cell #7 was switched on in the final part of the experiment essentially having the scope (any particular attention was reserved to the charging protocol) to obtain other elements to understand the effect of a change of gas composition, due to electrolysis, on the mechanism of a supposed contamination by air. In fact, in this case, the line was continuously

![Figure 5](image-url)

**Figure 5**

Time chart of the electrolysis current applied to the cells reported in Table I
fluxed by the carrier gas since more than 700 h. 4He data of cell #7 are shown elsewhere in this book (28). The maximum value of heat power excess in each cell was found in the range from 2 to 19 W (± 10%) and the ratio $\Gamma = \frac{\text{excess power}}{\text{input power}}$ ranging from 0.13 to 0.70. These figures and other ones extracted from the plots above are reported in Table III.

Table III. Summary of the calorimetric results

<table>
<thead>
<tr>
<th>Cell #</th>
<th>Cathode diameter mm</th>
<th>Treatment</th>
<th>*Current density mA cm$^{-2}$</th>
<th>&amp;Excess Power W</th>
<th>Vol.Exc Power W cm$^{-3}$</th>
<th>Surf.Exc. Power W cm$^{-2}$</th>
<th>$\Gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2</td>
<td>no</td>
<td>1280</td>
<td>10.0±1.0</td>
<td>111</td>
<td>6.4</td>
<td>0.26</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>yes</td>
<td>460</td>
<td>2.0±0.2</td>
<td>3</td>
<td>0.46</td>
<td>0.13</td>
</tr>
<tr>
<td>8</td>
<td>3</td>
<td>yes</td>
<td>947</td>
<td>15.0±1.5</td>
<td>79</td>
<td>7.1</td>
<td>0.43</td>
</tr>
<tr>
<td>10</td>
<td>3</td>
<td>no</td>
<td>905</td>
<td>19.0±1.9</td>
<td>100</td>
<td>8.6</td>
<td>0.70</td>
</tr>
</tbody>
</table>

*Current density at the maximum excess power
&Maximum excess power
Figure 7: Cell #4
Upper figure. $^4$He concentration in the gas stream of cell #4 and reference cell #1
Bottom figure. Left ordinate: input power; Right ordinate: heat power excess

Figure 8: Cell #8
Upper figure. $^4$He concentration in the gas stream of cell #8 and reference cell #1
Bottom figure. Left ordinate: input power; Right ordinate: heat power excess
Tritium data

Tritium data are reported in figs. 10 and 11. In both fig. 11 five equal graphs are reported in which each of them gives $q_{th}^*$, as calculated by eqn. 12, $q_{exp}^*$ measured in the recombined gases (we remind that $q_{exp}^* = x_{th}^*$) and only the values of the difference $(q_{exp}^* - q_{th}^*)$ satisfying the condition $(q_{exp}^* - q_{th}^*) \geq \frac{\Delta x_e}{x_e} = \frac{5}{80} = 6.25 \times 10^{-2}$, where $\Delta x_e$ is the experimental error on the measurement, given in dpm ml$^{-1}$, of the atomic fraction of tritium in the recombined D$_2$O. In considering the plot of cell#1, it has to be taken into account that the theoretical equation has been calculated by assuming $\alpha_E$(Pt) = $\alpha_E$(Pd). Since, notwithstanding the criterion adopted before in discriminating $(q_{exp}^* - q_{th}^*)$ values, some $(q_{exp}^* - q_{th}^*)$ values were still found > 0, to be conservative, the quantity of tritium atoms in excess in the electrolytic solution of each cell was obtained by subtracting the averaged data $(q_{exp}^* - q_{th}^*) > 6.25 \times 10^{-2}$. To calculate the integral curve of the excess of tritium atoms, the following equation was then used:

$$\int_{0}^{t} \frac{1}{3}H \, dt = 9.17 \times 10^6 \alpha_{E}x_{e}V_{o}\left\{ \int_{0}^{t} \left[ (q_{exp}^* - q_{th}^*) - (q_{exp}^* - q_{th}^*) \right] \, dt \right\}$$

(16)
Figure 10
Tritium in recombined gases. Values of $q_{th}$, $q_{exp}$ and $(q_{th}-q_{exp})$ for cells #1, #2, #4, #8 and #10.
by considering first that the combination of $\alpha_E$ and $q$ allows to write $x^* = \alpha_E x^q$ (see also the list of symbols and constant). As it clearly appears in fig. 11, through the procedure adopted, excess of tritium is present only in cells #2 and #8.

Figure 11
Excess of tritium atoms for cells #2 and #8

Neutrons data
In this experiment, there was no statistical evidence of neutron emission from the cells. Fig. 12 shows the number of neutrons detected each ten minutes by the groups of tubes no. 1, 3, 6, 11, 12 before and during the experiment.

Figure 12
Counts in 10 min of 5 counting groups out of 12 before and after the starting of the experiment. For checking the positioning of the counting groups, see figure 4
The neutron countings vs time graphs of the other groups are not shown for readability purposes, but they show similar characteristics and trend. As shown in the figure, there is no statistical difference between the number of neutrons detected when the electrolysis was in progress and the background. Apparent exceptions are the two large countings of the group 12, which occurred between ~900 and ~1200 hours. However, simple considerations about the settlement of the experimental apparatus together with the check, by the oscilloscope, of the pulses coming from the groups of tubes, showed that the two great enhancements of the neutron counting rate of the group 12 (as well other enhancements detected by other groups not showed in fig. 12 and having the same characteristics), were not generated by neutrons. In fact:
- As shown in fig. 4, the presence of two rings of groups of tubes surrounding the toroid embedding the cells, assures that a bunch of neutrons coming from whichever cell (and also from the region outside the detector) must hit at least one group in each ring. Enhancements of the neutron counting of group 12, if generated by real neutrons, must hence be simultaneous to other enhancements of at least one of the outer ring groups. Particularly, the group 11 is bounded to detect an enhancement too;
- The normal shape of the analogical signal coming from a group hit by a neutron, as checked by the oscilloscope, is a peculiar negative shape (see fig. 6 of ref. 24). The two enhancements of the neutron counting detected by the group 12 were instead generated by anomalous pulses, in which a sudden, very large, negative drop of the signal was followed by oscillations around zero.

Discussion
Due to the absence of significant amount of neutrons and low excess of $^3$H atoms with respect to the excess power measured we will try in the followings to consider the nuclear reaction

$$d + d = ^4\text{He} + 23.8 \text{MeV(lattice)}$$  \hspace{1cm} (17),

as originating the observed power excess. Therefore the most important comparison to be made is that between the power excess and the $^4\text{He}$ found assuming the above reaction as the source of both these quantities. In order to compare the excess power data reported in figures 6 to 9 with $^4\text{He}$ found, it is necessary to evaluate the minimum sampling time, $mst$, defined as the time required to fill our sampling cylinder of volume $V_s$ at the gas flow-rate $J_G$ at the sampling stage (after the catalytic recombination). The $mst$ quantity is given by:

$$mst = \frac{V_s}{J_G} = \frac{PV_s}{RT_s \left( f_{n_t} + \frac{3}{4} (1 - \eta) I \right) RT}$$  \hspace{1cm} (18)

The quantity so calculated corresponds to the time which would be spent by an ideal piston moving at constant velocity from the bottom to the top of the sampling cylinder. This is like to say that the entering gas moves pushing out the pure $\text{N}_2$ initially present in the cylinder. Under this hypothesis, the composition
of the gas trapped in the cylinder at sampling is representative of the gas composition during the last \( mst \) seconds before the sampling independently of the fluxation time. In fig. 13 (right scale), the equation 18 is reported vs the electrolysis current at different values of \( \eta \). It appears that in the range of our experimental conditions the \( mst \) value is confined within a short range of variability and, in any case, is at least 12 times lower than the sampling time we effectively adopted because of the reasons shown elsewhere (28). As expected from eqn. 18, for \( \eta \to 1 \), \( mst \) is independent of the electrolysis current value. Therefore, if the heat power excess is measured in the gas phase, by considering the mass flux balance in the cell it is possible to calculate the expected \(^4\text{He} \) concentration, \( x_{\text{He}} \), produced through reaction 17, in the sampled gas stream by the equation below:

\[
x_{\text{He}} = \frac{P_{\text{exc}}}{N_A} \int_0^t \frac{q_t}{N_A} P_{\text{exc}} dt = \frac{P_{\text{exc}}}{N_A} \int_0^t \left[ f_{\text{He}} + \frac{3}{4F} (1 - \eta) I \right] dt
\]

The approximate term implies \( P_{\text{exc}} \) constant on time in the integration interval and the contribution of \(^4\text{He} \) flux negligible with respect the sum of the other fluxes. From eqn. 19, one sees that the \(^4\text{He} \) concentration measurable in the gas stream depends on some experimental parameter which is mandatory to keep under control. In fig. 13 (left scale), the quantity \( \frac{\partial x_{\text{He}}}{\partial P_{\text{exc}}} \), derived from eqn. 19, is plotted against the electrolysis current. For \( \eta \to 1 \), also the specific \(^4\text{He} \) concentration becomes independent from \( I \).

![Figure 13](image)

**Left scale:** Specific \(^4\text{He} \) expected to be measured in the electrolysis gases per 1 W of excess power as function of electrolysis current at different values of \( \eta \).

**Right scale** (scatter plots): Minimum sampling time, \( mst \), as function of the electrolysis current \( \eta \) is the recombination yield.
To convert the experimental concentration values (in ppb) of $^4\text{He}$ into excess power, the following equation was used:

$$P_{\text{ex}} = 10^{-9} e n_{\text{at}} q_r x_{\text{at}} = 46.9788 x_{\text{at}}$$  \hspace{1cm} (20)

where $n_{\text{at}} = \frac{N_{\text{PV}}}{RT}$ is the total number of molecules in the sampling cylinder. $P_{\text{ex}}$ calculated by eqn. 20 has to be intended averaged on $mst$. In fig. 14, we give in separate plots for cell #4 and #10, respectively, top and bottom part of the figure.

![Graph showing heat power excess for Cell #4 and Cell #10 over time](image)

**Figure 14**

Upper figure: cell #4; Bottom figure: cell #10

Left ordinate: Heat power excess as measured by calorimetry. Continuous line

Right ordinate: Heat power excess calculated by $^4\text{He}$ data (reaction 17 and eqn.20). Circle points
the heat power excess, as obtained by calorimetry, left scale, (see figs. 7 and 9 bottom plots right scales), and on the right scale the heat power excess calculated by eqn. 20 through $^4$He data (see figs. 7 and 9 upper plots). It is important to observe that in each plot of fig. 14 the two heat power excess quantities, obtained in a completely independent way, are comparable (note that the limits of the ordinate scales are the same in each plot). It is evident by examining fig. 14 that two different processes are at work and in both cases the $^4$He concentrations are clearly higher than the respective $^4$He backgrounds before the start of the experiment (not for cell #10 because we have not background) other than the background found in the blank cell #1. If we limit to the time interval where electrolysis is still on (see fig. 5), we observe for cell #4 a progressive increase of the heat power excess from $^4$He, HPEH, to compare with a quite constant and low heat power excess from calorimetry, HPEC. This trend is clear even if the error bars are considered for both the quantities, though, quite at any time, ($HPEH \pm \Delta HPEH) = (HPEC \pm \Delta HPEC)$ holds. In cell #10, the result ($HPEH \pm \Delta HPEH) > (HPEC \pm \Delta HPEC)$ is always found only when the electrolysis current was drastically decreased or off. In all other cases, HPEC prevails. What is impressing is that $^4$He recovering is systematically found after generation of excess heat.

Concerning the evaluation of $\Delta HPEC$, this was already treated in the experimental section while the evaluation of $\Delta HPEH$ originates immediately from eqn. 20 being this quantity proportional to the error in the $^4$He determination (28). The application of eqn. 20 to the $^4$He data of cells #2 and #8 (figs. 6 and 8, respectively) leads to $HPEH$ values lower than $0.6 \pm 0.1$ W after subtracting the $^4$He background before the starting of the electrolysis. This value is in any case better (but comparable to) than the calorimetric detection limit as shown in Table II. According to fig. 13 and the maximum HPEC found, the corresponding maximum values of the $^4$He concentration expected for cells #2 and #8 should be, respectively, 195 and 292 ppb. This is far enough from the experimental findings. A similar reasoning better matches for cell #10 and partially also for cell #4. Therefore, apparently, we are left with the dilemma of one cell which shows a $^4$He concentration in the gas phase of the correct order of magnitude (with respect to the heat excess) while others, cell #2 and cell #8, do not. On the other hand it must be pointed out that before drawing any particular conclusion two central questions are to be answered: does it exist a time relation between the heat generation and $^4$He release out from the surface? and, if yes, is the delay a function of how the source is deep inside with respect to the electrode surface?

To our knowledge, there are not yet experimental evidences to answer satisfactorily to these questions. On the other hand some pieces of general information on this argument comes only from the experiments carried out for studying the effect of the $^3$He, as product of tritium decay, on mechanical and physical properties of materials candidate for hot fusion reactors (33). However, our hypothesis on the behaviour of helium in Pd when it is generated in situ is based on the fact that being highly insoluble, it nucleates everywhere a point or linear defect exists. The transformation from a cluster of a few atoms to microbubbles depends on the extension of the defects and/or to the possibility of migration of defects. The probability for a bubble to reach the surface is in any case very low and increases on decreasing the distance between the nucleation
centre and the surface. If this distance becomes greater than 10 nm (see M.W. Lee in ref. 16), the calculated time required for $^4$He to reach the surface could be as long as 14 years (34). Up to this point we believe this scheme applicable to all the metals and alloys, but things could seriously change in the case of a Pd specimen subject to a process where defects are continuously generated and propagate quite randomly in the metallic matrix due to D charging. In this case, the pattern for $^4$He to reach the surface could be through the defects (sometimes so extended that they collapse generating fractures) produced by D loading. If so, we can expect any time correlation between the time of heat generation and $^4$He release, except be made when the site of the nuclear reaction is the surface itself or some monolayers below. It appears that the recovery of $^4$He in the gas phase of different electrodes (and therefore different microstructures,) is far from being expected to occur at any definite and predictable rate. Therefore, under this hypothesis, all the results of heat excess and $^4$He we showed keep their own consistency.

For the above considerations, we have to expect that the condition $\text{HPEH} \leq \text{HPEC}$ should be commonly found. An experimental evidence consistent with the reasoning above comes from the literature (3) in which the energy associated to $^4$He was found more or less an order of magnitude lower than the energy found by calorimetry.

The integration of HPEH and HPEC data of cell #10 given in fig. 14 is reported in fig. 15 where throughout the experiment the heat excess from $^4$He is found comparable with the heat excess measured by calorimetry, though, the former is, in extended interval of time (from 200 to 500 h and from 600 to 1050 h), greater than the latter.

![Figure 15: Cell #10](image)

Left ordinate: Heat excess obtained by integration on time of heat power excess as measured by calorimetry (fig. 9 bottom figure right ordinate)
Right ordinate: Heat excess obtained by integration on time of eqn.20
According to the reasoning above this is not allowed and we have to introduce in the discussion the possibility of another source of ⁴He, likely, air contamination in some extent as it appears from the ⁴⁰Ne detection (28).

Concerning the error bar on solid curve of fig. 15, the same considerations given before for the other curves containing calorimetric data still hold.

Concerning tritium data it should be noted that in the plots of fig. 10 and 11 there are a few number of experimental points, $q_{\text{exp}}$, not only exceeding the expected value, $q_{\text{th}}$, over the experimental error, but $\geq 1$. It is easy to demonstrate from eqn 13 that the condition $q_{\text{lim}} \geq 1$, in absence of tritium generation, would produce the result $\frac{\alpha_f}{\alpha_v} \leq 1$ which is clearly impossible due to the fact that $\alpha_f$ must be $>1$ and $\alpha_v \equiv 1$. This constitutes a strong rigorous support in favor of generation of tritium, even if, this seems to occurs at low level and sporadically.

On the other hand, it is important to remind that the tritium measurement is not an on-line measurement and since it is done on the recombined $D_2O$, the minimum time interval between two samplings is the time necessary to produce at least 1 ml of $D_2O$ which is the suitable volume to perform the tritium determination. This time is given by $\frac{2F_i}{\nu i \eta}$. By considering the current plots (see fig. 5), the time required varies from $\approx$1 (at $I=2.5$ A) to $\approx$33 (at $I=0.1$A) hours. For practical reasons is not possible for us to perform the tritium test every 1 ml of $D_2O$ produced, especially at the highest current values, so very often the sampling (of 1 ml) is made on a higher volume of $D_2O$. In the case of spike-wise release of tritium in the cell, as it is likely expected, this implies to loose this time structure because of the dilution effect which flats the concentration profile.

Further key point to take into consideration, often not sufficiently stressed in discussing tritium measurements, is the distribution of tritium generated, if any. It is our opinion, also supported in literature (35,36), that tritium should be mostly searched in the cathode and/or in the gas phase. In fact, if tritium is produced in the bulk of the cathode, it can be trapped and/or released on time as DT (g). If generated at the surface, the DT molecules go directly in the gas phase. According to the general adopted mechanism (37) of H (D) electrolytic reduction on a cathode, $Me$, the $H_2 (D_2)$ formation step can follow two different processes:

$$D_{\text{ads}}(Me) + D_{\text{ads}}(Me) = D_2 (g) \tag{21A}$$

and/or

$$D_{\text{ads}}(Me) + D_2O + e(Me) = D_2 (g) + OD^- \tag{21B}$$

If tritium atoms, $T$, are produced, at the $Me$ surface, reactions 21 become:

$$D_{\text{ads}}(Me) + T_{\text{ads}}(Me) = DT (g) \tag{22A}$$

and/or

$$T_{\text{ads}}(Me) + D_2O + e(Me) = D_2 (g) + OT^- \tag{22B}$$

---

7Without invoking the concurrent release of both $^4$He and $^{20}$Ne
Through step 22B, it is possible to keep tritium in the solution as really found and reported previously (20,24,25). There is not other process allowing to tritium to remain in the solution in significative extent being the solubility of DT in D2O and the catalyzed reaction of T at the cathode with dissolved oxygen in solution to give DTO, very negligible processes. Therefore, a complete balance of tritium would require its measurement in both the Pd cathode and the solution. Furthermore, as we did, the tritium is measured in the gas phase via the external catalytic recombination two factors does exist which concur to give a result in defect: i ) the isotopic effect on the catalytic recombination which increases the rate of the D2O formation with respect to DTO; ii ) the stoichiometric ratio \( \frac{D_2}{O_2} \), fixed by the electrolysis and good for the recombination, is no more strictly satisfied in the recombinator when tritium is generated.

From fig. 11, it appears that a net production of tritium atoms, significatively out of the experimental errors (we remind the procedure showed in the results section) only occurs in the cells #2 and #8. Incidentally, in these cells \(^4\)He was found to be very low and not comparable with the excess heat.

If the channel of tritium of the plasma fusion \( d,d \) reaction is invoked, we can calculate that the energy released throughout the experiment in the case of cell #2, for instance, is 115 J, whereas, a rough evaluation of the integrated heat excess measured by calorimetry in the same cell (see fig. 6) is more than four order of magnitude higher. By the same reasoning, we should expect an excess of neutrons with respect to the background equal to the number of tritium atoms. This would imply a maximum averaged rate of \( \approx 7 \times 10^7 \text{ ns}^{-1} \). This rate value other than to be very dangerous, it would be easily detectable whereas, as shown in fig. 12 no excess of neutrons above the background was measured.

Conclusions

Our calorimetric results show excess power quite in linea with the other positive results reported up to now. In particular, if one considers the power excess per unit electrode surface area as a function of the current density, a fair agreement is found with the general behaviour first pointed out by Storms (38) by considering many calorimetric measurements on the Pd- D2O electrolysis carried out at room temperature in different laboratories with different calorimetric devices and procedures were used. As concerns the nuclear products, in the present experiment, a lack of neutrons and a low tritium excess on two cells out of four has been observed contrarily to what expected on the basis of \( d,d \) reactions. Also, under this respect our results do confirm the previous findings which exhibited such a large unbalance. As for the \(^4\)He measurements in the escaping gases, the detection of \(^{20}\)Ne (28), prevents to draw definite conclusions from the comparison with the calorimetric data. However it cannot be left unnoticed the notable commensurate amounts of \(^4\)He and heat excess found in the case of cell #10. Quite striking is also the time pattern of the amount of \(^4\)He recovered which, shifted in time, does match the power excess time pattern observed. The different quantities of \(^4\)He recovered from different cells (e.g. #8 and #10) where power excesses of same order of magnitude have been observed, if understandable by invoking different kinetics of the \(^4\)He release, highlight the
usefulness of being able to perform a complete energy and mass balance by taking into account also the $^4$He content of the electrodes.

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APPENDIX A

**List of Symbols**

- $\alpha_E$: electrolytic separation factor $\equiv \frac{x_E}{x}$
- $\alpha_V$: isotopic separation factor in the vaporization $\equiv \frac{x_V}{x}$
- $a_D$: activity of D$_2$ in the gas phase
- $a_i$: intercept of the calibration curve of the i-th cell W
- $b_i$: slope of the calibration curve of the i-th cell W °C$^{-1}$
- $C_g$: heat capacity of D$_2$O vapour J (mol K)$^{-1}$
- $C_l$: heat capacity of D$_2$O liquid J (mol K)$^{-1}$
- $C_r$: relative capacity of Pd sponge trap
- $C_S$: heat capacity of solution J (mol K)$^{-1}$
- $C_{trap}$: nominal capacity of Pd sponge trap for D$_2$ mol
- $d$: deuterium nuclei m m
- $d$: inner diameter of cell mm
- $f_{D_2O}$: feed of D$_2$O to the cell moli s$^{-1}$
- $f_G$: gas flow-rate of the gas mixture moli s$^{-1}$
- $f_{N_2}$: N$_2$ flow-rate scm$^{3}$s$^{-1}$
- $f_{cond}$: correction for D$_2$O condensation in recombinator cm$^{3}$s$^{-1}$
- $\Gamma$: ratio of excess power on input power cm$^{3}$s$^{-1}$
- $h$: height of the solution level in the cell mm
- $h$: recombination yield
- $I$: electrolysis current A
- $k_{Pyrex}$: heat conductivity constant of Pyrex W (m K)$^{-1}$
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{Rad}$</td>
<td>Stefan Boltzmann constant ( W m^{-2} K^{-4} )</td>
</tr>
<tr>
<td>$L$</td>
<td>heat of evaporation of $D_2O$ ( J \text{ mol}^{-1} )</td>
</tr>
<tr>
<td>$l$</td>
<td>thickness of Pyrex wall of the cell ( mm )</td>
</tr>
<tr>
<td>$M$</td>
<td>molar mass of $D_2O$ ( g \text{ mol}^{-1} )</td>
</tr>
<tr>
<td>$M_{Pd}$</td>
<td>atomic mass of Pd ( g \text{ mol}^{-1} )</td>
</tr>
<tr>
<td>$m_S$</td>
<td>mass of solution ( mol )</td>
</tr>
<tr>
<td>$m_{st}$</td>
<td>minimum sapling time ( s )</td>
</tr>
<tr>
<td>$n_{D_2O}$</td>
<td>number of moles of $D_2O$ in $V^o$</td>
</tr>
<tr>
<td>$n_{m}$</td>
<td>total number of molecules in $V_s$</td>
</tr>
<tr>
<td>$P$</td>
<td>Atmospheric pressure ( kPa )</td>
</tr>
<tr>
<td>$p$</td>
<td>vapour pressure of $D_2O$ ( Pa )</td>
</tr>
<tr>
<td>$p_{D_2}$</td>
<td>$D_2(g)$ partial pressure ( Atm )</td>
</tr>
<tr>
<td>$P_{exc,i}$</td>
<td>excess of heat power of the $i$-th cell ( W )</td>
</tr>
<tr>
<td>$P_{in}$</td>
<td>input power ( W )</td>
</tr>
<tr>
<td>$P_{out}$</td>
<td>output power ( W )</td>
</tr>
<tr>
<td>$q_r$</td>
<td>energy released by reaction 17 ( MeV )</td>
</tr>
<tr>
<td>$r$</td>
<td>correlation factor in linear regression</td>
</tr>
<tr>
<td>$p_1$</td>
<td>density of $D_2O$ ( kgm^{-3} )</td>
</tr>
<tr>
<td>$t$</td>
<td>time constant ( s )</td>
</tr>
<tr>
<td>$T_r$</td>
<td>temperature of room ( ^\circ C )</td>
</tr>
<tr>
<td>$T_s$</td>
<td>temperature of solution ( ^\circ C )</td>
</tr>
<tr>
<td>$T^o_s$</td>
<td>temperature of solution at $P_{in} = 0$ ( ^\circ C )</td>
</tr>
<tr>
<td>$T_{tb}$</td>
<td>temperature of thermostated bath ( ^\circ C )</td>
</tr>
<tr>
<td>$T^o_{tb}$</td>
<td>temperature of thermostated bath at $P_{in} = 0$ ( ^\circ C )</td>
</tr>
<tr>
<td>$V$</td>
<td>voltage of the cell ( V )</td>
</tr>
<tr>
<td>$v_{cons}$</td>
<td>volume of $D_2O$ consumed by electrolysis ( cm^3 )</td>
</tr>
<tr>
<td>$v_{rec}$</td>
<td>volume of $D_2O$ recombined ( cm^3 )</td>
</tr>
<tr>
<td>$v$</td>
<td>molar volume of $D_2O$ ( cm^3 \text{ mol}^{-1} )</td>
</tr>
<tr>
<td>$V_s$</td>
<td>volume of the sampling bottle ( cm^3 )</td>
</tr>
<tr>
<td>$V_{th}$</td>
<td>thermoneutral potential ( V )</td>
</tr>
<tr>
<td>$V^o$</td>
<td>volume of solution in the cell ( cm^3 )</td>
</tr>
<tr>
<td>$w_{Pd}$</td>
<td>weight of Pd sponge in the trap ( g )</td>
</tr>
<tr>
<td>$x$</td>
<td>atomic fraction of DTO in $D_2O$ ( \text{cm}^3 \text{ mol}^{-1} )</td>
</tr>
<tr>
<td>$x_{D_2O}$</td>
<td>atomic fraction of DTO in $D_2O$ feed</td>
</tr>
<tr>
<td>$x_{He}$</td>
<td>atomic fraction of $^4$He in the gas mixture</td>
</tr>
<tr>
<td>$x_{T}$</td>
<td>atomic fraction of T in the gas mixture</td>
</tr>
<tr>
<td>$x^o$</td>
<td>starting atomic fraction of DTO in the electrolyte</td>
</tr>
<tr>
<td>$y$</td>
<td>D/Pd atomic ratio</td>
</tr>
<tr>
<td>$\Delta H^o$</td>
<td>standard enthalpy change of formation of $D_2O_1$ ( kJ \text{ mol}^{-1} )</td>
</tr>
<tr>
<td>$\Delta H_{abs}$</td>
<td>enthalpy change of reaction 8 ( kJ \text{ mol}^{-1} )</td>
</tr>
<tr>
<td>$\Delta S^o_{abs}$</td>
<td>standard entropy change of reaction 8 ( J \text{ mol}^{-1}K^{-1} )</td>
</tr>
<tr>
<td>$\Delta T_i$</td>
<td>$\Delta T_i = (T_i - T^o_i) - (T^o_{tb} - T^o_{tb})_i$ ( ^\circ C )</td>
</tr>
</tbody>
</table>
APPENDIX B

List of constants

\( \alpha_E \) electrolytic separation factor \quad 1.8
\( \alpha_V \) isotopic separation factor in vaporization \quad \approx 1
\( C_g \) heat capacity of \( \text{D}_2\text{O} \) vapour \quad 44.500 J (mol K\(^{-1}\))
\( C_l \) heat capacity of \( \text{D}_2\text{O} \) liquid \quad 84.349 J (mol K\(^{-1}\))
\( C_{\text{Drap}} \) nominal capacity of Pd sponge trap \quad 0.47 D\(_2\) moles
\( d \) inner diameter of cell \quad 22.0 mm
\( e \) elementary charge \quad 1.60219\times10^{-19} C
\( F \) Faraday constant \quad 96484.6 C mol\(^{-1}\)
\( f_{\text{N}_2} \) \( \text{N}_2 \) flow-rate \quad 0.54 scm\(^3\)s\(^{-1}\)
\( h \) height of the solution level in the cell \quad 180 mm
\( k_{\text{Pyrex}} \) heat conductivity constant of Pyrex \quad 0.878 W (m K\(^{-1}\))
\( k_{\text{Rad}} \) Stefan Boltzmann constant \quad 5.6703\times10^{-8} Wm\(^2\)K\(^{-4}\)
\( L \) heat of evaporation of \( \text{D}_2\text{O} \) \quad 41.673 kJ mol\(^{-1}\)
\( l \) thickness of Pyrex wall of the cell \quad 2 mm
\( M \) molar mass of \( \text{D}_2\text{O} \) \quad 20.02748 g mol\(^{-1}\)
\( M_{\text{Pd}} \) atomic mass of Pd \quad 106.42 g mol\(^{-1}\)
\( N_A \) Avogadro number \quad 6.02205\times10^{23} mol\(^{-1}\)
\( P \) Atmospheric pressure \quad 101.3 (nominal) kPa
\( p \) vapour pressure of \( \text{D}_2\text{O} \) \quad 7.83\times10^2\exp(5.143\times10^{-2}\text{T}_S) \text{ Pa}
\( P_{\text{DTO}} \) vapour pressure of DTO \quad 7.66\times10^2\exp(5.165\times10^{-2}\text{T}_S) \text{ Pa}
\( q_r \) energy released by reaction 17 \quad 23.8 MeV
\( R \) ideal gas constant \quad 8.31441 J (mol K\(^{-1}\))
\( r_l \) density of \( \text{D}_2\text{O} \) \quad 1.1055 g cm\(^{-3}\)
\( T_r \) temperature of room \quad 20±1 °C
\( T_{\text{tb}} \) temperature of thermostated bath \quad 21.0±0.1 °C
\( V \) molar volume of \( \text{D}_2\text{O} \) \quad 18.116 cm\(^3\) mol\(^{-1}\)
\( V_{\text{s}} \) volume of the sampling bottle \quad 500 cm\(^3\)
\( V_{\text{th}} \) thermoneutral potential \quad 1.53668 V
\( V^* \) volume of solution in the cell \quad \approx 53 cm\(^3\)
\( x^* = x_f \) starting atomic fraction of DTO in the electrolyte \quad 80 \( ^{8}\)dpm ml\(^{-1}\)
\( y \) \( \text{D}/\text{Pd} \) atomic ratio (at 298 K, \( \text{PD}_2 = P \)) \quad 0.67
\( \Delta H^\circ \) standard enthalpy change of formation of \( \text{D}_2\text{O}_1 \) \quad 296.53 kJ mol\(^{-1}\)
\( \Delta H_{ab} \) enthalpy change of reaction 8 \quad \Delta H_{ab}(y) = 95.5 - 89.96y \text{ kJ mol}\(^{-1}\)
\( \Delta S_{ab}^\circ \) standard entropy change of reaction 8 \quad 106.3 J mol\(^{-1}\)K\(^{-1}\)

\[ ^8[\text{dpm} = 1 \text{ disintegration per min} = 9.17\times10^6 \text{ atomi T min}^{-1} = 4.50\times10^7 \mu\text{Ci}] \]