

Evidences for Associated Heat Generation and Nuclear Products Release in Palladium Heavy-Water Electrolysis.

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Summary. — In a galvanostatic experiment of charging deuterium in a palladium cathode, nuclear and thermal effects were found. A sintered palladium electrode shaped as a parallelepiped was used. After six days of electrolysis at 200 mA/cm², a simultaneous emission of neutrons, tritium excess in the electrolytic solution and temperature rapid increase were observed. During the event which lasted 4 minutes, we estimated an emission of $7.2 \cdot 10^6$ neutrons while the electrode temperature reached 150 °C. Excess of tritium was evaluated to be $(2.14 \pm 0.04) \cdot 10^{11}$ atoms. If the energy released as heat, 176 J, is compared with the energy associated to the d+d reactions, 0.1 J, three orders of magnitude are still defective. Electrode characterization after the events is reported.

PACS 25.88 – Fusion reactions

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PACS 82.45 – Electrochemistry and electrophoresis.

1. – Introduction.

In the light of FP[1] and Jones *et al.*[2] papers, we try to perform experiments of so-called «cold fusion» through the electrolytic reduction of deuterium at a palladium cathode.

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Up to now we have carried out two experiments and others, in a multiple-cell set-up, are planned. Though we have not yet understood the reasons of the different results found between the two experiments, we believe of some interest to report our phenomenological evidences of associated nuclear and thermal effects found only in the first experiment. This confirms that even if the experimental conditions under control are the same, the results are not reproducible showing that some key parameters are still not controlled. The experimental procedure differs from that used in ref. [1] in the following points:

- i) a sintered palladium electrode was used instead of a cast metal electrode;
- ii) temperature of the electrode was measured instead of the temperature of the electrolyte solution;
- iii) calorimetric measurements were not carried out.

For the detection of nuclear phenomena, neutron and gamma emission were monitored and the tritium contained in the solution before and after the electrolytic process has been measured.

2. - Experimental.

A parallelepiped electrode was shaped in a stainless steel die by pressing at 2200 kg/cm² palladium sponge powder (Johnson & Mathey) with average grains size of about 1 μm. X-ray fluorescence analysis carried out in the powder as received showed traces of Sb and Pt. XRD analysis did not show any other phase except that of metallic palladium with sharp lines indicating a high degree of crystallinity of the powder sponge supplied. The compacted specimen was then sintered in a high-vacuum furnace at 900 °C for 10 hours and cooled to room temperature at 5 °C/min under high-vacuum. The final dimensions and density of the specimen were, respectively, (6 × 5 × 25) mm³ and 80.5% of the bulk Pd.

The specimen was subsequently machined at one end in such a way as to house a glass-protected S-type thermocouple, and then joined to a glass tube by an epoxy adhesive which also avoids any contact between air and palladium cathode.

The natural gamma emitter content of the electrode was measured with a HP germanium counter in a low background cell used for environmental measurements. No difference with the background was found. The same result has been obtained by measuring the electrode two days after the end of the experiment.

As shown in fig. 1, the electrolysis was carried out in a three-electrode cell with a cylinder Pt gauze as counter electrode and Hg/HgO/OD⁻ (0.1 M) electrode as reference electrode.

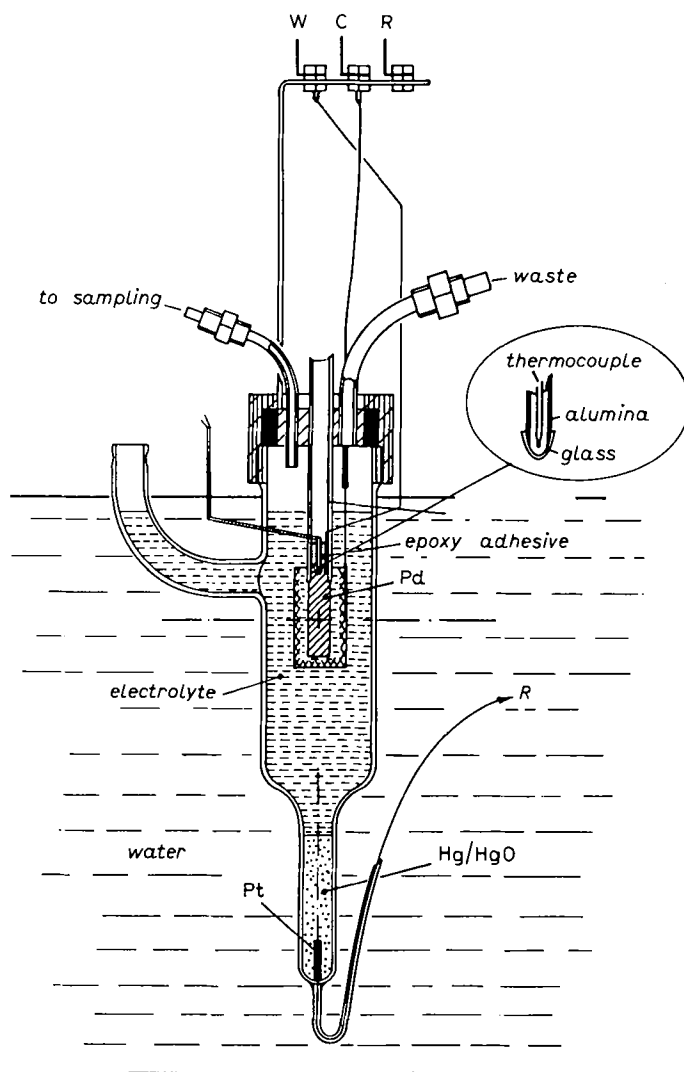


Fig. 1. - Electrolytic cell assembly.

Up to 41 ml of LIOD 0.1 M solution in D_2O at 99.8% were used to fill the glass cell. Through a lateral U-tube, D_2O was added regularly in order to replace D_2O consumed by the electrolysis. A total volume of 19 ml of D_2O was added during the experiment. In this way both the Pd and Pt electrodes were completely immersed in the electrolytic solution with 10 mm of solution above their tops.

Around the cell, placed in a water bath, the neutron and γ -ray detectors were positioned as shown in fig. 2.

As a monitor of neutron emission, a dose equivalent detector consisting of a 3He gas filled proportional counter surrounded by a spherical polyethylene

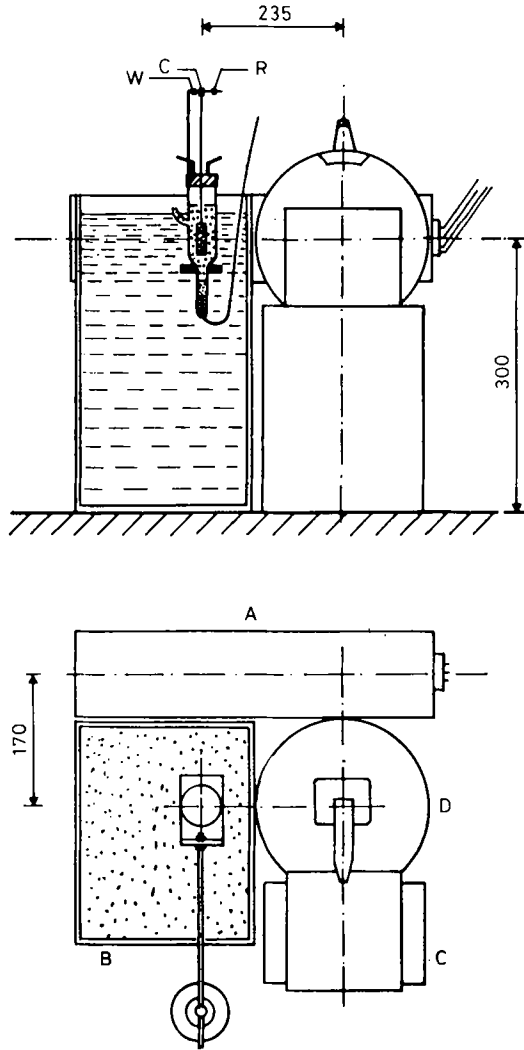


Fig. 2. - Neutron and γ -ray detectors positioning. A: NaI(Tl) monocrystal, B: water bath, C: He^3 neutron counter with polyethylene sphere moderator D.

moderator [3] was used. The pulse output of the monitor was sent to a scaler for integral counting and to a recorder. The consistency between the integral counts on the scaler and the spikes recorded has been checked and perfect agreement has been always found provided the counting rate was such that the interval between counts was maintained larger than the inertial time of the pen of the recorder. Check of the neutron detector, dose equivalent monitor, was made according to the manufacturer instructions and in such a way the consistency of counting rate with the expected value was verified by means of different calibrated Am-Be sources. A linear response in counting rate with the activity of

the source was checked up to a counting rate of 3200 counts/s from a calibrated source delivering $2.5 \cdot 10^6$ neutrons/s continuously distributed in time.

Total (intrinsic plus geometrical) efficiency of the detector has been measured by positioning a calibrated Am-Be source at the same distance from detector as the palladium electrode. A value of $5 \cdot 10^{-5}$ has been found for neutron spectrum of the Am-Be source.

The neutron background level, in the experimental set-up used, has been measured for several days. The distribution of the counts hour rate showed a typical Poisson distribution with (3.0 ± 0.2) counts/h as medium value. To check the behaviour of the counter against thermal effect, the air surrounding the counter was warmed up to 80 °C for a long time with no appreciable effect on the counting rate. Other checks were made against sources of electromagnetic noise that could have been activated during the measurement.

A high-efficiency NaI(Tl) rectangular block $4'' \times 4'' \times 16''$ was used to monitor gamma emission. Signals were analyzed for energy determinations through a SILENA spectrum analyzer. Energy calibration of the system was set to collect gamma energies up to 5 MeV. Data were continuously cumulated for each run of the measurement.

Time, electrode temperature, palladium electrode potential *vs.* reference and the potential difference between Pt and Pd electrodes, were simultaneously transferred into a computer. The data acquisition system was programmed, for safety reasons, to switch off the applied current when the electrode temperature was over 80 °C.

The tritium content of a sampled volume of the initial solution, of the heavy water added and of the final solution was measured with a Beckmann LS 1801 liquid scintillation system.

Measurements were always taken with a narrow window open on the tritium energy interval and with a large window open from 0 to about 2 MeV. No significative difference between the two measurements has been found, confirming the correct assignment of the tritium radioactivity. Chemiluminescence effects due to the lithium content in the solution, though very low, were properly corrected.

3. – Results and discussion.

After some preliminary measurements with different cell geometries, in light-water, at several current density values and, also, by modulating the current [4], we started on April 20th by imposing a constant current density of 200 mA/cm². After 150 hours, a nuclear and thermal effect was recorded simultaneously, as shown in fig. 3.

In a time interval of 22h 5' 54", 116 counts were displayed by the neutron counter signal scaler while on the neutron recording we were able to count 80

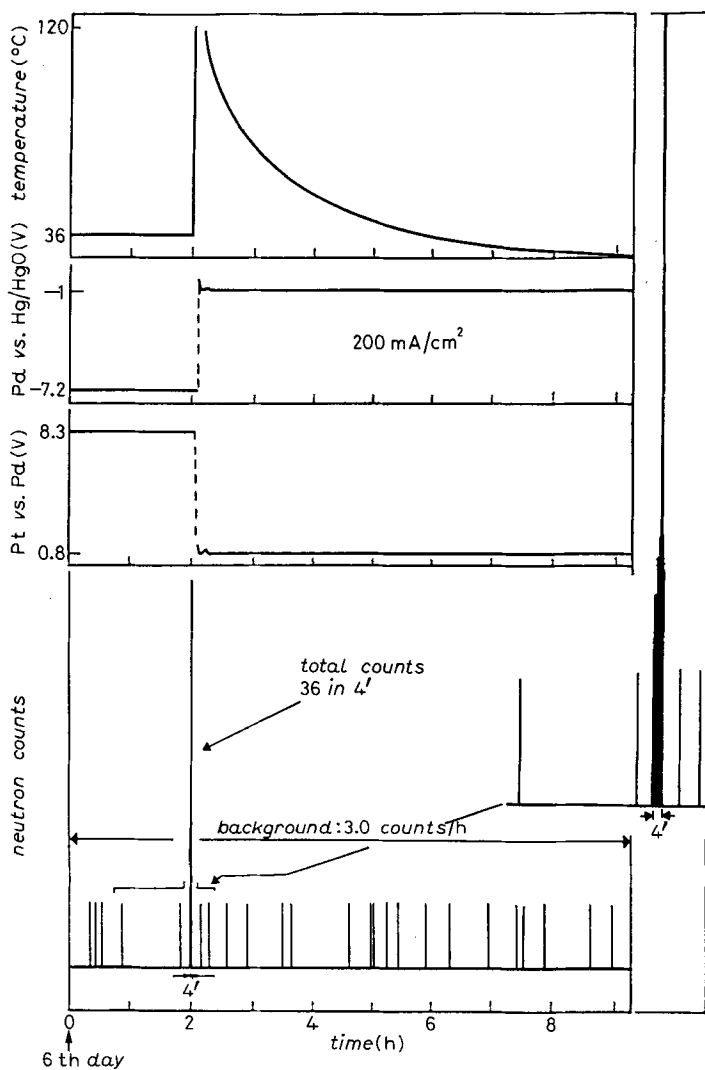


Fig. 3. - Recordings of the experimental variables during the event.

single spikes only. An unresolved group of spikes which lasted about 4 minutes was recorded, while a sudden increase of the electrode temperature was occurring.

Before and after the event, the neutron counting rate was equal to the background level, while at least 36 counts were concentrated in the unresolved group, where the neutron emission was at least 180 times the background level.

Taking into account the quoted efficiency, the 36 counts imply an emission of $7.2 \cdot 10^5$ neutrons in 4 minutes, *i.e.* $3 \cdot 10^3$ n/s. Due to the very low counting rate (0.15 counts/s) during the reported event, in comparison with the maximum

counting rate for which the counter was checked (3200 counts/s), the only reason for the inadequate efficiency, and, consequently, total neutron emission reported, may be found in a neutron emission in form of intense bursts, each of them separated by a few tens of seconds.

Figure 4 shows the temperature recording in which both the maximum temperature reached, as obtained by extrapolating the cooling and heating curve, and the rate of the temperature increase have been, respectively, estimated and measured.

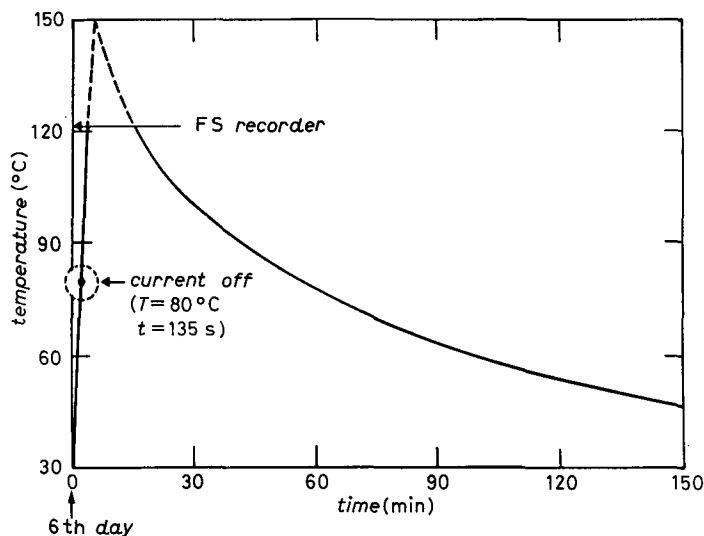


Fig. 4. - Temperature trend of the palladium electrode during the event.

If the time of $t = 135$ s is taken as the current off time (see fig. 4), we estimate that the neutron emission was maintained for other 105 s, while the electrode temperature continued to increase, up to reach a value of 150°C .

Electrolyte solution partially evaporated and some milliliters were found condensed in the silicon waste tube. Due to this, the Pd and Pt electrodes were found to be not fully covered by the electrolytic solution.

In fact we repeatedly determined that at 200 mA/cm^2 the experimental D_2O consumption rate was 0.345 ml/h compared to the theoretical value obtained by Faraday's laws, of 0.326 ml/h . The difference has to be attributed to the continuous loss of heavy water by the D_2O -saturated gas phase escaping from the cell. If the time between the last D_2O addition and the event and the cell cross-section are taken into account, we calculated that, at the event time, the electrodes were still covered by at least 6 mm of the electrolytic solution.

From these findings, the final volume of the solution was calculated and used for the tritium balance as reported below. We were not able to resolve the time

of the temperature and neutron effects in such a way as to decide which of the two effects occurred first.

Six hours about after the event, current was switched on again, still at the same current density, for 15 hours without adding D₂O. No significant event was observed.

The second experiment was continuously carried out from May 20th to the end of June following the same experimental procedure but adding new instrumentation for γ -ray (HP Ge detector and background rejection) and neutron (BF₃ detector) detection with separated data acquisition systems.

Due to the tritium content in the heavy water used (2 000 d.p.m./ml) and to its consumption during the electrolytic processes, the assessment about excess of tritium in the solution, as a consequence of the reported event, needs a complete balance of the tritium added, found in the electrolytic cell and released by the process.

The release of tritium in the gas phase during the electrolytic process has been measured in two blank experiments. We have runned an electrolytic process with a platinum cathode allowing a passage of 43 650 Coulombs, the negative balance of tritium has been found of $(5\,900 \pm 890)$ d.p.m. As second blank we can use the result of the negative (with respect to neutron and heat emission) second experiment with a palladium cathode prepared as described before. In this case, after a passage of 942 564 Coulomb the negative balance of tritium was of $(154 \pm 1) \cdot 10^3$ d.p.m. Initial solution volumes used were essentially the same to those used in the first palladium positive experiment except for the volumes released in the electrolytic process that are proportional to the charge passed through the cell. Both these negative balances are an underestimation of the real value of the tritium released in the case of the experiment in which heat and neutron emission have been measured, due, on the one hand to the difference in the electrolytic separation factors between platinum and palladium and, on the other hand, to the use, for a part of the process, of heavy water with lower content of tritium. When the balance is made by taking into account the tritium put into the electrolytic cell, the one found in the solution at the end of the process and the one delivered by the process itself, according to the two blank results, scaled by the different charge used, we found a positive balance of tritium respectively of (255 ± 40) becquerel and (381 ± 8) becquerel corresponding to $(1.43 \pm 0.22) \cdot 10^{11}$ and $(2.14 \pm 0.04) \cdot 10^{11}$ atoms of tritium in excess. All the quoted errors are to be considered as 2σ errors. The discrepancy of the two blank experiments caused the two different lower limits for the tritium excess. The tritium excess was also found in electrochemical experiments by other authors [5-7].

We are not able at this stage to assess if the tritium excess found is representative of the all tritium produced due to the fact that tritium could be present both in the cathode and/or in the escaping gas phase. Recent results give a ratio of 100 between tritium found in the gas phase and in solution [8].

Some analyses were performed on the electrode after the event. XRD and X-ray fluorescence spectra were carried out on the electrode surface showing, respectively, a PdD_{0.706} phase with a lattice parameter of 0.402 nm (compared to PdH_{0.706} with a lattice parameter of 0.396 nm as given by the crystallographic index handbook) and traces of Hg and Sn other than Pt and Sb already present in the starting material. The presence of Hg and Sn are well explained in terms of electrolytic reduction, both of mercury ion coming from the HgO solubility equilibrium in the reference electrode, and tin contained as impurity in HgO itself.

Due to the short length of the event with respect to the γ -ray spectrum integration time (22h 5' 54"), no statistical significant difference was observed with respect to the γ -ray background spectrum.

According to ref. [9], in the energy interval measured by the NaI counter, two regions could be interested by gammas coming as by product of nuclear fusion reactions. Protons coming from $d + d \rightarrow p + T$ channel induce Coulomb excitations of Pd isotopes resulting in emission of gammas from $2^+ \rightarrow 0^+$ de-excitation with energy in the interval from 0.37 to 0.56 MeV. Taking into account the excess of tritium detected, the branching ratio of the associated gamma emission [9, 10] and the geometrical counter efficiency, the resulting total count less than 10^{-5} times the background counts, in the same energy interval, and is even smaller than its only statistical error. Neutrons coming from $d + d \rightarrow n + {}^3\text{He}$ channel after moderation may suffer radiative capture and γ emitted detected by NaI counter. With a calibrated neutron source placed in the experimental set-up in the same position as the palladium cathode we have found, in an energy interval centered around 2.22 MeV, 60 counts/s for a source of $2.5 \cdot 10^4$ neutrons/s.

For the reported event this should result in an excess of $1.6 \cdot 10^8$ counts respect to a measured background integrated over the time measurements of $3.6 \cdot 10^6$ counts and just comparable to the statistical error.

In order to clarify the heat generation, we believe that it is important to establish if lithium plays a role at nuclear or electrochemical level or both. Anyway, whether or not lithium can be incorporated into palladium during the electrolysis, becoming competitive with D in occupying the interstitial sites, could be of relevant interest.

Two ways were undertaken to do this on two parts of our electrode: i) etchings dissolving each time quite uniform layers of the sample; ii) vaporization of lithium from the sample using the high-temperature Knudsen cell-mass spectrometric technique.

A mixture of nitric and hydrochloric acid (1 : 3 in volume) was used to etch two times the sample solubilizing, respectively, 0.296 and 0.345 g of the electrode material. In this way, two layers of the electrode were dissolved, respectively, 0.43 and 1.29 mm thick both measured from the original surface. Lithium content was measured by flame emission spectroscopy in the two corresponding

solutions and it was found to be, respectively, 356 and 50 p.p.m. X-ray fluorescence spectrum on the surface of the sample after the second etching showed pure Pd only, if some metallic impurities, contained in the chemicals used in the etching solution, were not taken into account. It is important to point out that Hg was not present, therefore, lithium found has to be considered not incorporated in the porous metallic matrix *via* permeation through the pores as liquid solution but it is present at that distance from the surface by a solid-state diffusion mechanism originated by the electrolytic reduction of lithium.

Confirmation of this also comes through the other independent technique used. According to the literature[11], the Knudsen-cell mass spectrometry allows to measure both the equilibrium fugacity of a vaporizing species from a solid phase and the thermodynamic activity, when the measured fugacity is divided by the fugacity of the same vaporizing component taken in a reference state (for instance, pure lithium in this case).

Two runs were carried out on two quite similar portions of the available sample: the first one on the sample portion as received and the second run on the other portion which was machined in such a way as to wear away a layer of about 1 mm. In all cases only monoatomic lithium was found to constitute the gas phase in equilibrium over the sample. In the first run, we obtained ${}^7\text{Li}$ pressures from $6.3 \cdot 10^{-3}$ to $1.5 \cdot 10^{-1}$ Pa in the temperature range from 823 to 1598 K, while, in the second run we found that ${}^7\text{Li}$ pressures were from $5.6 \cdot 10^{-4}$ to $1.3 \cdot 10^{-3}$ Pa corresponding to a temperature interval from 1136 to 1534 K. If these pressure values are compared to the corresponding metal lithium pressures, we have a strong evidence that the lithium activity in Pd is very low and decreasing going from the surface to the bulk. For example, the lithium activity, at 1400 K goes from $6 \cdot 10^{-6}$ to $9 \cdot 10^{-8}$. The presence of lithium in Pd electrode is consistent with the Li-Pd phase diagram [12] and confirms that, after the electrolytic reduction, the incorporation of Li in the Pd lattice *via* solid-state diffusion, is a process occurring at a significant rate with respect to the rate of the recombination with D_2O which is expected to be higher as it is peculiar for an alkaline metal. At this stage we cannot say which role is played by lithium but the fact that Li is found constitute an *a priori* condition for a possible role played by lithium metal.

Due to the high rate of the temperature increase (see fig. 4), the palladium electrode can be considered, at least in the initial part, as an adiabatic system and as a rough approximation we can assume an overall temperature change of 100°C . By taking into account the electrode mass and the palladium specific heat, 176 J were produced in 240 s about corresponding to a specific power released of 1.2 W/cm^3 .

The estimated neutron emission accounts for $\approx 7 \cdot 10^5 \text{ d} + \text{d} \rightarrow {}^3\text{He}$ (0.82 MeV) + n(2.45 MeV) reactions. Taking into account that the energy left in the cathode is essentially that released by the ${}^3\text{He}$, this channel contributes with 10^{-7} J . The tritium excess found accounts for $\approx 2 \cdot 10^{11} \text{ d} + \text{d} \rightarrow {}^3\text{H}$ (1.01 MeV) + p (3.03 MeV) reactions; this channel contributes $\approx 10^{-1} \text{ J}$.

These results show that: *a)* the two reactions, at the deuteron energy that is relevant for the conditions of our experiments, must have very different cross-sections; *b)* the estimated heat produced is three orders of magnitude higher than that resulting from the measured reaction products.

We wonder whether a careful theoretical and computational analysis of the reactions at low energy in the light of an «Oppenheimer-Phillips process» [13, 14] could give some clarification for the first result. The second result calls either for an inefficiency of our tritium production estimation of $\approx 10^{-3}$ or for the fundamental importance in the heat generation of different processes or mechanisms. If the results of ref. [8] are taken into account a difference of an only one order of magnitude does exist between heat and reaction products.

Part of the results here described was presented in the special session on Cold Fusion at the Meeting of the Electrochemical Society, Los Angeles, May 8th and at «Workshop on Cold Fusion Phenomena» in Santa Fé, May 22-25th.

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Redears wishing to correspond should refer to S. Frullani for the nuclear aspects of the paper, and to D. Gozzi for the other aspects.

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● RIASSUNTO (*)

In un esperimento galvanostatico di caricamento di deuterio in un catodo di palladio, sono stati osservati effetti nucleari e termici. È stato usato un elettrodo di palladio sinterizzato a forma di parallelepipedo. Dopo sei giorni di elettrolisi a 200 mA/cm², è stata osservata simultaneamente una emissione di neutroni ed un rapido incremento della temperatura dell'elettrodo; un eccesso di trizio è stato trovato nella soluzione elettrolitica dello stesso esperimento. Durante l'evento, durato 4 minuti, abbiamo stimato una emissione di 7.2×10^5 neutroni mentre la temperatura dell'elettrodo ha raggiunto 150°C. L'eccesso di trizio è stato stimato in $(2.14 \pm 0.04) \times 10^{11}$ atomi. L'energia rilasciata come calore, 176 J, è di tre ordini di grandezza superiore a quella, 0.1 J, associata ai prodotti della reazione d+d. Viene riportata infine una caratterizzazione dell'elettrodo dopo l'evento.

(*) Traduzione a cura della Redazione.

Резюме не получено.