

TIME-DELAYED APPARENT EXCESS HEAT GENERATION IN ELECTROLYSIS FUSION EXPERIMENTS

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In many recent electrolysis fusion experiments, excess heat, tritium, and neutron production have been reported as intermittent bursts. These burst phenomena are described in terms of a surface reaction mechanism involving hysteresis of deuterium solubility in palladium as a function of the metal temperature. Excess heat generation is shown to be attributable to a hitherto neglected time-delayed chemical process due to the solubility hysteresis of deuterium in palladium. Negative results of no apparent excess heat generation from light-water electrolysis experiments is attributed to the fact that the solubility hysteresis of hydrogen occurs at a higher temperature range than that for deuterium. Apparent excess heat generation is expected to be also observable in blank electrolysis experiments with light water at higher pressures.

The reported results¹ of excess heat,²⁻¹¹ neutron,⁸⁻¹³ and tritium^{8, 9, 14, 15} generation from heavy-water electrolysis experiments with palladium cathodes are burst phenomena: i.e., these are reaction products which were observed intermittently in bursts, and are not reproducible at present.¹⁶⁻¹⁸ Furthermore, the deuterium fusion rate inferred from the observed excess power^{2,3} is at least twelve orders of magnitude larger than that inferred from the observed neutron counting rates.¹² In this paper, the reported result of apparent excess heat generation²⁻¹¹ is described in terms of a hitherto neglected time-delayed chemical process which can occur during solubility hysteresis¹⁹ of deuterium in palladium.

In many electrolysis experiments, excess (~ 10%) heat generation as originally reported by Fleischmann and Pons^{2,3} has been observed as bursts. Calculations and experiments based on ordinary chemical explanations are shown²⁰ to account for no more than ~ 1% excess power. The observed rate of excess heat generation corresponds to a deuterium-deuterium (D-D) fusion rate of $\Lambda_{\text{exp}}^{\text{heat}} \approx 10^{-10} \text{s}^{-1}/D$, and is about thirteen orders of magnitude larger than the inferred neutron production rate of $\Lambda_{\text{exp}}^n \approx 10^{-23} \text{s}^{-1}/D$ as originally reported by Jones *et al.*¹² A surface fusion mechanism²¹ consistent with conventional nuclear physics was recently proposed to explain the results of electrolysis experiments.²⁻¹⁵ The effect of a deuteron velocity distribution in the context of the surface reaction mechanism was shown²² to be very important in reducing the discrepancy between the electrolysis fusion results and the conventional estimates of cold fusion rates. More recently, it has been suggested²¹ and

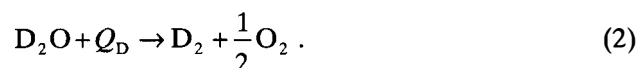
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shown²³ that the effect of electron screening further reduces this discrepancy and that $\Lambda^{\text{exp}} \approx 10^{-23}\text{s}^{-1}/D$ may therefore be explainable within the context of conventional nuclear physics. However, the D-D fusion rate of $\Lambda^{\text{heat}} \approx 10^{-10}\text{s}^{-1}/D$ cannot at present be explained by conventional nuclear physics.²³ Many speculative nuclear fusion theories¹ have been proposed to account for the observed rate of excess heat generation, but none are satisfactory to account for both the excess heat and the corresponding nuclear products.

During electrolysis of heavy water, the input power P_i (in watts, W) is given by

$$P_i = I\Delta V, \quad (1)$$

where I and ΔV are the electric current (in amperes, A) and the potential difference (in volts, V) across the two electrodes. Part of the input power, P_D , given by Eq. (1), is dissipated in the dissociation of heavy water molecules



With the dissociation energy $Q_D \approx 70$ kcal/mole $\text{D}_2 \approx 4.87 \times 10^{-19}$ J/ D_2 the power dissipated by reaction (2) is

$$P_D = 1.53 I(\text{in A})W \quad (3)$$

corresponding to a rate of D_2 molecule production (via reaction (2)) of

$$R_D = (0.3125 \times 10^{19}) I(\text{in A}) \text{D}'_2 \text{ s/s}. \quad (4)$$

The rest of P_i , P_R , is dissipated as thermal energy by Joule heating of the electrolysis cell (heavy water, electrodes, etc.). The conservation of energy requires that

$$\int P_i dt = \int (P_D + P_R) dt \quad (5)$$

in absence of any additional chemical or nuclear reactions. If this were true for the electrolysis experiments,^{2-10, 17, 18} the conservation of energy on a local time basis would approximately require

$$P_i(t) \approx P_D(t) + P_R(t), \quad (6)$$

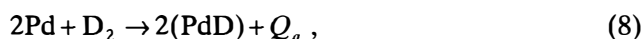
where $P_R \approx 2P_D$ in a typical electrolysis experiment.¹⁰ The excess power, ΔQ , is defined as

$$\Delta P(t) \approx [P_D(t) + P_R(t)] - P_i(t). \quad (7)$$

$\Delta P(t) \neq 0$ then implies a violation of the approximate conservation of energy, Eq. (6). In an open electrolysis system,^{2-5, 8-10, 17, 18} $P_i(t)$ and $P_D(t)$ (which is not measured since recombination of D_2 and O_2 is avoided) are evaluated using Eqs. (1) and (3), respectively, while $P_R(t)$ is determined by calorimetric measurements. In a closed electrolysis system,^{6, 10} $P_i(t)$ is evaluated by Eq. (1), while both $P_R(t)$ and $P_D(t)$ (by catalytic recombination of D_2 with O_2 , i.e., inverse of reaction (2)) are determined by calorimetric measurements.¹⁰

Measurement of the solubility of deuterium in palladium (Pd) was first made in 1935 by Sieverts and Zapf.²⁴ A more comprehensive series of measurements of deuterium solubility in palladium was carried out by Sieverts and Danz¹⁹ in 1936. Their plot of isobaric solubilities at 740 mm Hg is shown in Fig. 1. In electrolysis experiments, three stages may occur based on Fig. 1; these are described in the following.

- (a) Initial Absorption Stage: During the initial stage of electrolysis of heavy water, the deuterium gas produced by reaction (2) on the surface of the Pd cathode is absorbed into Pd via the reaction



where $Q_a \approx 9$ kcal/mole $\text{D}_2 \approx 37.7$ kJ/mole $\text{D}_2 \approx 6.26 \times 10^{-20}$ J/ D_2 .

The enthalpy or heat of solution relative to the gas phase for hydrogen absorption in Pd have been measured to be -19 kJ/mole H_2 and -46 kJ/mole H_2 , for the α and β phases of Pd, respectively.^{25,26} For a typical ($\alpha + \beta$) mixed phase with $\text{H}/\text{Pd} \leq 0.5$, it is about -9 kcal/mole $\text{H}_2 \approx -38$ kJ/mole H_2 .²⁷ Heats of desorption (endothermic) are similar to heats of solution (exothermic) except for an opposite sign.²⁷ The heat of absorption and desorption for deuterium in Pd is expected to be very similar to those for hydrogen in Pd. Thus, Q_a in Eq. (8) will be assumed to be $Q_a = 38$ kJ/mole D_2 in the following. At 25°C , D_2 can be loaded into Pd up to $\text{D}/\text{Pd} \approx 0.66$ corresponding to a deuteron density of $n_{\text{D}_2}(25^\circ\text{C}) \approx n_{\text{D}}/2(25^\circ\text{C}) \approx 0.66n_{\text{Pd}}/2 \approx 2.23 \times 10^{22}$ D'_2/cm^3

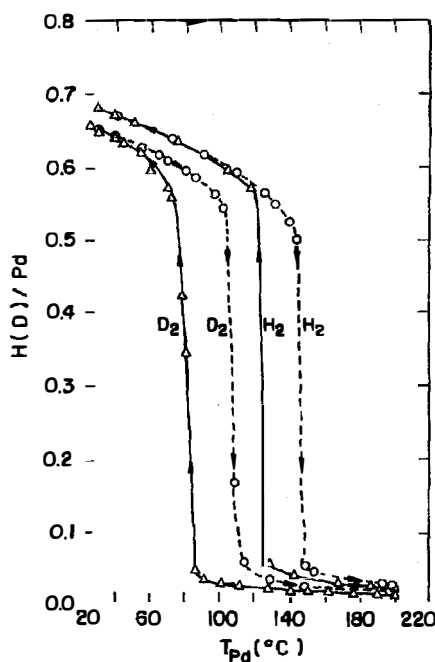


Fig. 1. Isobaric solubilities¹⁹ of hydrogen and deuterium in palladium as a function of the palladium temperature, T_{Pd} , at gas pressure of 740 mm Hg.

using $n_{\text{Pd}} \approx 6.767 \times 10^{22} / \text{cm}^3$. Therefore, a total energy of $Q_a n_{\text{D}_2} \approx 1.40 \text{ kJ/cm}^3 \text{ Pd}$ can be produced from reaction (8) by loading D_2 into Pd from $\text{D/Pd} = 0$ to $\text{D/Pd} \approx 0.66$.

- (b) **Desorption Stage:** As can be seen from Fig. 1, deuterium solubility in Pd has separate (hysteresis) desorption and reabsorption stages. As the temperature, T_{Pd} , of Pd is increased from $T_{\text{Pd}} \approx 103^\circ\text{C}$ to 113°C , the D/Pd ratio decreases rapidly from $\text{D/Pd} \approx 0.55$ to $\text{D/Pd} \approx 0.06$ by desorbing deuterons. Since the deuterium desorption process from Pd is endothermic, the Pd is cooled and T_{Pd} decreases during this stage, leading to the following stage (c).
- (c) **Reabsorption Stage:** As T_{Pd} decreases from $\sim 86^\circ\text{C}$ to $\sim 73^\circ\text{C}$, the D/Pd ratio increases rapidly from ~ 0.05 to ~ 0.56 by the absorption of deuterium into Pd. Since deuterium absorption by Pd is exothermic, the Pd is heated and T_{Pd} increases during this stage. The increase of T_{Pd} during stage (c) helps to re-initiate stage (b) which may in turn lead back to stage (c). This hysteresis cycle, (b) \rightleftharpoons (c), can repeat many times during electrolysis experiments as demonstrated recently by Arata and Zhang¹¹ from their experimental measurements of T_{Pd} as a function of time during electrolysis of heavy water with a large Pd cathode.

During the initial stage (a), D_2 's produced by reaction (2) will be slowly absorbed into Pd via reaction (8) at a rate $R_a \approx R_D$, since a clean Pd surface provides favorable conditions for the dissociation of the D_2 molecules. If D_2 's are absorbed at the rate $R_a = R_D$ given by Eq. (4), then heat is produced via reaction (8) at a rate of

$$P_a = Q_a R_D = 0.196 I (\text{in A}) W \quad (9)$$

as compared with $P_D = 1.53 I (\text{in A}) W$, Eq. (3). The time ΔT_a required for loading D_2 into a Pd volume V_{Pd} is

$$\Delta T_a = V_{\text{Pd}} Q_a n_{\text{D}_2} / P_a = V_{\text{Pd}} n_{\text{D}_2} / R_a . \quad (10)$$

During ΔT_a , P_a will contribute to $\Delta P(t)$, Eq. (7), as an additional excess power. After time ΔT_a , $P_a = 0$ and so $\Delta P(t) = 0$ for long periods (for days and weeks) if T_{Pd} is kept constant and no additional effects happen after initial loading is complete.

However, T_{Pd} increases during and after the initial absorption stage (a) described above (e.g., by Joule heating through P_R and heat released by D desorption), the stored D's in the Pd will begin to be desorbed. The rate of desorption is expected to be slow until the desorption stage (b) is reached. In the recent electrolysis experiment by Arata and Zhang,¹¹ the desorption time δt for the desorption stage (b) is shown to be $\delta t \approx 80$ seconds and the hysteresis cycle time (or duty cycle) Δt is about $\Delta t \approx 10$ min for a large Pd cathode of 2 cm diameter and 5 cm height (a total volume of $\sim 15.7 \text{ cm}^3$).¹¹ The desorption time δt and the hysteresis duty cycle Δt will depend on experimental conditions such as external cooling efficiency and the size of the Pd cathode.

During the desorption stage (b) of the hysteresis cycle, $\tilde{n}_{\text{D}_2} \approx f n_{\text{D}_2}$ (2.23×10^{22}) f D_2 's/ cm^3 are desorbed from the Pd cathode during a short time period, δt , where $f \leq 1$

due to the possibility of hysteresis scan.²⁸ D_2 is desorbed from Pd at a rate faster¹¹ than R_D , $R_a^{(b)} > R_D$, creating a non-equilibrium situation. D_2 gas bubbles may form a D_2 gas layer that virtually covers the Pd cathode, thereby allowing the formation of a high-intensity double-layer electric field which is enhanced at the sharp tips of surface asperities (or whiskers).²⁹ This electric field can be $\sim 10^9$ V/m along with a high (D_2^+) current I_B , even though the voltage across the electrolysis cell is only ~ 1 V.²⁹ Spark discharge currents due to dielectric breakdown of gases are known to occur in short gaps ($\sim 10^{-7}$ cm) with potentials ~ 1 V.³⁰ For the above non-equilibrium situation, the electric current I is not expected to be 100% efficient for electrolysis of D_2O . Instead, P_D given by Eq. (3) is reduced to $P_D^{(b)} = 1.53 I_D$ (in A) $W = P_D - \delta P_D$ where I_D is an effective dissociation current, $I_D = I - I_B$. Joule heating will then be increased by $\delta P_R \approx \delta P_D$, i.e., $P_R^{(b)} = P_R + \delta P_R$. The local-time energy conservation relation, Eq. (7), is now modified to become

$$\Delta P^{(b)}(t) = [(P_D - \delta P_D) + (P_R + \delta P_R) + (Q_D - Q_a)R_a^{(b)}] - P_i, \quad (11)$$

where $Q_D R_a^{(b)}$ is the power produced from recombination of O_2 with D_2 desorbed from Pd for a closed system ($Q_D R_a^{(b)} = 0$ for an open system) and $-Q_a R_a^{(b)}$ is the power loss due to the (endothermic) desorption of D_2 from Pd. For the open system, $(P_D - \delta P_D)$ is assumed to be P_D (i.e., $\delta P_D \approx 0$) by experimentalists, and hence Eq. (11) reduces to

$$\Delta P_{\text{open}}^{(b)}(t) \approx \delta P_R - Q_a R_a^{(b)} \quad (11a)$$

using $P_i = P_D + P_R$. Therefore if $\delta P_R > Q_a R_a^{(b)}$, $\Delta P_{\text{open}}^{(b)}(t) > 0$ will appear as an apparent excess power for the open system. If $\delta P_R < Q_a R_a^{(b)}$, $\Delta P_{\text{open}}^{(b)}(t) < 0$ will appear as an apparent power deficit for the open system. Both excess power and power deficit have been observed in a recent open-cell electrolysis experiment.¹⁰ For the closed system, Eq. (11) with $P_i = P_D + P_R$ and $\delta P_D \approx \delta P_R$ reduces to

$$\Delta P_{\text{open}}^{(b)}(t) \approx (Q_D - Q_a)R_a^{(b)} > 0 \quad (11b)$$

which appears as an excess power.

After desorption stage (b) described above is terminated, reabsorption stage (c) sets in. However, efficient reabsorption of D_2 into Pd will not start until T_{Pd} decreases below $\sim 80^\circ\text{C}$. Even after T_{Pd} drops below $\sim 80^\circ\text{C}$, the reabsorption rate $R_a^{(c)}$ will be much slower than that of the initial absorption stage (a), $R_a \approx R_D$, since the Pd surface is no longer clean. The local-time energy conservation relation, Eq. (7), is now modified to be

$$\Delta P^{(c)}(t) = [P_D + P_R + (Q_a - Q_D)R_a^{(c)}] - P_i \quad (12)$$

until Pd is saturated with D_2 , and after D_2 saturation, $\Delta P^{(c)}(t) = \Delta P(t)$, Eq. (7). For the open system, Eq. (12) reduces, with $P_i = P_D + P_R$ and $Q_D R_a^{(c)} = 0$, to

$$\Delta P_{\text{open}}^{(c)}(t) \approx Q_a R_a^{(c)} > 0 \quad (12a)$$

before D₂ saturation, and $\Delta P_{\text{open}}^{(c)}(t) = 0$ after D₂ saturation. For the closed system, Eq. (12) reduces to

$$\Delta P_{\text{closed}}^{(c)} = (Q_a - Q_D)R_a^{(c)} < 0 \quad (12b)$$

before D₂ saturation, and $\Delta P_{\text{closed}}^{(c)} = 0$ after D₂ saturation. The apparent power deficit, $\Delta P(t) < 0$, as in the case of Eq. (12b) has been observed in a recent closed-cell electrolysis experiment.¹⁰ If $R_a^{(c)}$ is sufficiently slow and $(Q_a - Q_D)R_a^{(c)}$ is comparable to or less than the experimental uncertainty of $\sim 1\%$ of P_i , (i.e., $(Q_a - Q_D)R_a^{(c)} \lesssim 0.01 P_i$), then the apparent power deficit $\Delta P_{\text{closed}}^{(c)}(t) < 0$, Eq. (12b), may not be observable.

The non-equilibrium situation created by the hysteresis cycle is expected to be different for different experimental conditions (applied voltage and current, variation of Q_a in Eq. (8), size of the Pd cathode, size of electrolysis cell, surrounding cooling equipment and materials, methods of supplying additional heavy water, etc.) and hence it is very difficult to duplicate the same non-equilibrium condition. This may explain the non-reproducibility²⁻¹⁸ of the claimed excess heat generation²⁻¹¹ and nuclear fusion products⁸⁻¹⁵ in electrolysis experiments.

In the following, the results of excess power ($\sim 11\%$ of P_i with an experimental uncertainty of 3%) observed in an open cell by Scott *et al.*¹⁰ are discussed for a specific application of the local-time conservation relation (Eqs. (11), (11a), (12), and (12a)). The dimension of their Pd cathode is 0.55 cm diameter \times 8 cm corresponding to a Pd volume of $V_{\text{Pd}} \approx 1.9 \text{ cm}^3$ and a surface area of 14.06 cm². The corresponding applied current is $I = (600 \text{ mA/cm}^2)(14.06 \text{ cm}^2) = 8.44 \text{ A}$, so that $\Delta V = 4.74 \text{ V}$ if $P_i \approx 40 \text{ W}$. Before desorption stage (b), $\Delta P(t) \approx 0$ as discussed previously. During desorption stage (b), we assume $\Delta P_{\text{open}}^{(b)}(t) = \delta P_D - Q_a R_a^{(b)} \approx 7 \text{ W}$ from Eq. (11a). If $R_a^{(b)} \approx R_D$ is assumed, $\delta P_D \approx 8.65 \text{ W}$ since $Q_a R_D \approx 1.65 \text{ W}$. The effective dissociation current I_D is then $I_D = 8.44 \text{ A} - (8.65/1.53) \text{ A} \approx 2.79 \text{ A}$, and $(P_D - \delta P_D) \approx 1.53 I_D W \approx 4.27 \text{ W}$ compared with $P_D \approx 1.53(8.44) \text{ W} = 12.91 \text{ W}$. The desorption time $\Delta T^{(b)}$ is then $\Delta T^{(b)} \approx f n_{\text{D}_2} V_{\text{Pd}} / R_a^{(b)} \approx f n_{\text{D}_2} V_{\text{Pd}} / R_D \approx 1.605 \times 10^3 f \text{ sec.} \approx 26.8 f \text{ min.}$ During reabsorption stage (c), $\Delta P_{\text{open}}^{(c)} = Q_a R_a^{(c)} \approx Q_a R_D \approx 1.65 \text{ W}$ (from Eq. (12a)) and $\Delta T^{(c)} \approx \Delta T^{(b)} \approx 26.8 \text{ min.}$, if $R_a^{(c)} \approx R_a^{(b)} \approx R_D$. The hysteresis duty cycle is then $\Delta T = \Delta T^{(b)} + \Delta T^{(c)} \approx 54 \text{ min.}$ for $f \approx 1$. If the hysteresis cycles repeats twice, excess ($\sim 11\%$) heat of $\sim 4.3 \text{ W}$ (an average of 7W and 1.65W) lasting approximately two hours will be observed as in the experiment of Scott *et al.*¹⁰

In all of the reported electrolysis experiments except a few (Gozzi *et al.*,⁸ and Arata and Zhang¹¹), the temperature T_{Pd} of the Pd cathode has not been directly measured as a function of time. Therefore, it is important to measure T_{Pd} in future electrolysis experiments in order to test the temporal correlation between T_{Pd} and the burst phenomena as predicted by the hysteresis effect.

For blank electrolysis experiments with H₂O, D-D fusion cannot occur. However, excess heat generation due to the hysteresis effect is still possible if T_{Pd} can be maintained between 120°C and 150°C, as can be seen from Fig. 1. Negative results (no apparent excess heat generation) for blank electrolysis experiments may be due to the fact that it is very difficult to maintain the hysteresis-cycle condition, 120°C $<$ T_{Pd} $<$ 150°C, at 1 atm. (or different hysteresis temperature ranges at different

pressures) in boiling water, especially with the small Pd electrodes that are commonly used in electrolysis experiments.^{2-7,9,10} To improve the reproducibility of the electrolysis experiments, the metal temperature must be maintained within the hysteresis-cycle temperature range. Blank electrolysis experiments with H₂O at higher pressures are expected to produce apparent excess heat since the hysteresis temperature range becomes lower at higher pressure.

Another important aspect of the desorption stage (b) during the hysteresis cycle is the fact that D₂'s generated from (b) can form a thin layer of D₂ gas on the Pd surface, creating a strong double-layer field²⁹ which can accelerate the D₂⁺ (and D⁺) ions produced by ionization and dissociation of D₂ molecules.²¹⁻²³ The accelerated D₂⁺ (and D⁺) ions with a statistical velocity distribution²² can impinge on the deuterated target in the Pd cathode, producing D-D fusion products as bursts at an enhanced rate²¹⁻²³ during each hysteresis cycle. Fusion bursts may occur for many repeated hysteresis cycles, as reported in various electrolysis experiments.⁸⁻¹⁵

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