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Preliminary note

Electrochemically induced nuclear fusion of deuterium

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INTRODUCTION

The strange behaviour of electrogenerated hydrogen dissolved in palladium has been studied for well over 100 years, and latterly these studies have been extended to deuterium and tritium [1]. For discharge of deuterium from alkaline solutions of heavy water we have to consider the reaction steps

$$D_2O + e^- \rightarrow D_{ads} + OD \quad \text{(i)}$$
$$D_{ads} + D_2O + e^- \rightarrow D_2 + OD \quad \text{(ii)}$$
$$D_{ads} \rightarrow D_{lattice} \quad \text{(iii)}$$
$$D_{ads} + D_{ads} \rightarrow D_2 \quad \text{(iv)}$$

It is known that at potentials negative to + 50 mV on the reversible hydrogen scale, the lattice is in the β-phase, hydrogen is in the form of protons (as shown by the migration in an electric field) and is highly mobile ($D = 10^{-7}$ $cm^2\ s^{-1}$ for the α-phase at 300 K).

The overall reaction path of D_2 evolution consists of steps (i) and (ii) [2] so that the chemical potential of dissolved D^+ is normally determined by the relative rates of these two steps. The establishment of negative overpotentials on the outgoing interface of palladium membrane electrodes for hydrogen discharge at the ingoing interface [3] [determined by the balance of all the steps (i) to (iv)] demonstrates that the chemical potential can be raised to high values. Our own experiments with palladium diffusion tubes indicate that values as high as 0.8 eV can be achieved readily [4] (values as high as 2 eV may be achievable). The astronomical magnitude of this value can be appreciated readily: attempts to attain this level via the compression of D_2 [step (iv)] would require pressures in excess of 10^{26} atm. In spite of this high compression, D_2 is not formed; i.e. the s-character of the electron density around the nuclei is very low and the electrons form part of the band structure of the overall system. A feature which is of special interest and which prompted the present investigation, is the very high H/D separation factor for absorbed hydrogen and deuterium (see Figs. 4 and 6 of ref. 2). This can be explained only if the H^+ and D^+ in the lattice behave as classical oscillators (possibly as delocalised species) i.e. they must be in very shallow potential wells. In view of the very high compression and mobility of the dissolved species there must therefore be a significant number of close collisions and one can pose the question: would nuclear fusion of D+ such as

$$^2D + {}^2D \rightarrow {}^3T(1.01\ MeV) + {}^1H(3.02\ MeV) \quad \text{(v)}$$

or

$$^2D + {}^2D \rightarrow {}^3He(0.82\ MeV) + n(2.45\ MeV) \quad \text{(vi)}$$

be feasible under these conditions?

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EXPERIMENTAL

In the work reported here D^+ was compressed galvanostatically into sheet, rod and cube samples of Pd from 0.1 M LiOD in 99.5% D_2O + 0.5% H_2O solutions. Electrode potentials were measured with respect to a Pd-D reference electrode charged to the α-β-phase equilibrium. We report here experiments of several kinds:

(1) Calorimetric measurements of heat balances at low current densities (= 1.6 mA cm^{-2}) were made using a 2 mm × 8 cm × 8 cm Pd sheet cathode surrounded by a large Pt sheet counter electrode. Measurements were carried out in Dewar cells maintained in a large constant temperature water bath (300 K), the temperature inside the cell and of the water bath being monitored with Beckman thermometers. The Heavy Water Equivalent of the Dewar and contents, and the rate of Newton's law of cooling losses were determined by addition of hot D_2O and by following the cooling curves.

(2) Calorimetric measurements at higher current densities were carried out using 1, 2 and 4 mm diameter × 10 cm long Pd rods surrounded by a Pt wire anode wound on a cage of glass rods. The Dewars were fitted with resistance heaters for the determination of Newton's law of cooling losses; temperatures were measured using calibrated thermistors. Experiments with rods up to 2 cm in diameter will be reported elsewhere [5]. Stirring in these experiments [and in those listed under (1)] was achieved, where necessary, by gas sparging using electrolytically generated D_2. Measurements at the highest current density reported here (512 mA cm^2) were carried out using rods of 1.25 cm length; the results given in Table 1 have been rescaled to those for rods of 10 cm length.

(3) The spectrum of γ-rays emitted from the water bath due to the (n, γ) reaction

$$^1H + n(2.45\ MeV) = {}^2D + \gamma(2.5\ MeV) \qquad \text{(vii)}$$

was determined using a sodium iodide crystal scintillation detector and a Nuclear Data ND-6 High Energy Spectrum Analyzer. The spectrum was taken above the water immediately surrounding an 0.8 cm × 10 cm Pd-rod cathode charged to equilibrium; it was corrected for background by subtracting the spectrum over a sink (containing identical shielding materials) 10 m from the water bath.

The neutron flux from a cell containing a 0.4 × 10 cm Pd-rod electrode was measured using a Harwell Neutron Dose Equivalent Rate Monitor, Type 95/0949-5. The counting efficiency of this Bonner-sphere type instrument for 2.5 MeV neutrons was estimated to be ≈ 2.4 x 10^{-4} and was further reduced by a factor ≈ 100 due to the unfavorable configuration (the rod opposite the BF_3-filled detector). The background count was determined by making measurements 50 m from the laboratory containing the experiments; both locations were in the basement of a new building which is overlain by 5 floors of concrete. In view of the low counting efficiency, counting was carried out for 50 h. Measurements on a 0.4 cm × 10 cm rod electrode run at 64 mA cm^{-2} gave a neutron count 3 times above that of the cosmic ray background.

(4) The rate of generation/accumulation of tritium was measured using similar cells (test tubes sealed with Parafilm) containing 1 mm diameter × 10 cm Pd-rod electrodes. Measurements on the D/T separation factor alone were made using an identical cell containing a 1 mm diameter × 10 cm Pt electrode (this measurement served as a blank as the H/D separation factors on Pd and Pt are known to be closely similar). 1 ml samples of the electrolyte were withdrawn at 2 day intervals, neutralised with potassium hydrogen phthalate and the T-content was determined using Ready Gel liquid scintillation "cocktail" and a Beckman LS 5000 TD counting system. The counting efficiency was determined to be about 45% using standard samples of T-containing solutions. The β-decay scintillation spectrum was determined using the counting system.

In these experiments, standard additions of 1 ml of the electrolyte were made following sampling. Losses of D_2O due to electrolysis in these and all the other experiments recorded here were made up by using D_2O alone. A record of the volume of D_2O additions was made for all the experiments.

In all of the experiments reported here all connections were fitted into Kel-F caps and the caps were sealed to the glass cells using Parafilm.

Results for the mass spectroscopy of the evolved gases and full experimental details for all the measurements will be given elsewhere [5].

RESULTS

Experiments (1) and (2)

In the calorimetric experiments we can set lower and upper bounds on the rates of Joule heating depending on whether reactions (i), (ii), and (iv) are balanced by

$$4OD^- \rightleftharpoons D_2O + O_2 + 4\,e^- \qquad \text{(viii)}$$

at the anode or by the reverse of reactions (i), (ii), and (iv). In the former case, the Joule heating is simply the cell current multiplied by (cell voltage -1.54 V), where 1.54 V is the cell voltage at which reactions (i), (ii) and (iv) balanced by (viii) are thermoneutral: irreversibilities in the electrode reactions and ohmic resistance losses have identical effects on the Joule heating. However, if reactions (i), (ii) and (iv) are reversed at the anode and, equally, if the reverse of reaction (viii) contributes to the cathode processes, then we get an upper bound to the Joule heating which is simply the cell current multiplied by the cell voltage.

TABLE 1

Generation of excess enthalpy in Pd cathodes as a function of current density and electrode size

Electrode Type	Dimensions /cm	Current density /mA cm^{-2}	Excess rate of heating /W	Excess specific rate of heating /W cm^{-3}
Rods	0.1 × 10	8	0.0075	0.095
		64	0.079	1.01
		512 [a]	0.654 [a]	8.33
	0.2 × 10	8	0.036	0.115
		64	0.493	1.57
		512 [a]	3.02 [a]	9.61
	0.4 × 10	8	0.153	0.122
		64	1.751	1.39
		512 [a]	26.8 [a]	21.4
Sheet	0.2 × 8 × 8	0.8	0	0
		1.2	0.027	0.0021
		1.6	0.079	0.0061
Cube	1× 1 × 1	125	WARNING! IGNITION? See text	
		250		

[a] Measured on electrodes of length 1.25 cm and rescaled to 10 cm.

We have confirmed in long duration experiments that the rates of addition of D_2O to the cells required to maintain constant volumes are those for reactions (i), (ii) and (iv) balanced by reaction (viii). Furthermore, subtraction of the ohmic potential losses in solution for the cell containing the large Pt anode shows that the electrolysis of D_2O is the dominant process, i.e. we have to assume that the Joule heating is close to the lower bound.

Table 1 gives the results for experiments designed to cover the effects of electrolyte geometry, electrode size, current density (or overpotential), method of operation, etc. The nature and large magnitude of the effects can be appreciated from the following observations:

(a) Excess enthalpy generation is markedly dependent on the applied current density (i.e. magnitude of the shift in the chemical potential) and is proportional to the volume of the electrodes, i.e. we are dealing with a phenomenon in the bulk of the Pd electrodes.

(b) Enthalpy generation can exceed 10 W cm^{-3} of the palladium electrode; this is maintained for experiment times in excess of 120 h, during which typically heat in excess of 4 MJ cm- 3 of electrode volume was liberated. It is inconceivable that this could be due to anything but nuclear processes.

(c) In research on thermonuclear fusion, the effects are expressed as a percentage of the break-even where 100% break-even implies that the thermal output equals the input (neglecting the power required to drive the equipment). In electrochemical experiments, we have in addition to take into account whether break-even should be based on the Joule heat or total energy supplied to the cell. Furthermore, in the latter case the energy supplied depends on the nature of the anode reaction. Table 2 lists three such figures of merit and it can be seen that we can already make reasonable projections to 1000%. Some of the factors important to scale-up are already apparent from Tables 1 and 2.

TABLE 2

Generation of excess enthalpy in Pd rod cathodes expressed as a percentage of break-even values. All percentages are based on $^2D + ^2D$ reactions, i.e. no projection to $^2D + ^3T$ reactions

Electrode Type	Dimensions /cm	Current density /mA cm^{-2}	Excess heating / % of break-even [a]	[b]	[c]
Rods	0.1 × 10	8	23	12	60
		64	19	11	79
		512	5	5	81
	0.2 × 10	8	62	27	286
		64	46	29	247
		512	14	11	189
	0.4 × 10	8	111	53	1224
		64	66	45	438
		512	59	48	839

[a] % of break-even based on Joule heat supplied to cell and anode reaction $4\ OD^- \rightarrow 2\ D_2O + O_2 + 4\ e^-$.
[b] % of break-even based on total energy supplied to cell and anode reaction $4\ OD^- \rightarrow 2\ D_2O + O_2 + 4\ e^-$.
[c] % of break-even based on total energy supplied to cell and for an electrode reaction $D_2 + 2\ OD^- \rightarrow 2\ D_2O + 4\ e^-$ with a cell potential of 0.5 V.

(d) The effects have been determined using D_2O alone. Projection to the use of appropriate D_2O + DTO + T_2O mixtures (as is commonly done in fusion research) might therefore be expected to yield thermal excesses in the range 10^5-10^6% (even in the absence of spin polarisation) with enthalpy releases in excess of 10 kW cm^{-3}. **We have to report here that under the conditions of the last experiment, even using D_2O alone, a substantial portion of the cathode fused (melting point 1544ºC), part of it vapourised, and the cell and contents and a part of the fume cupboard housing the experiment were destroyed.**

Experiment (3)

Figure 1A illustrates the γ-ray spectra which have been recorded in regions above the water bath adjacent to the electrolytic cells and this spectrum confirms that 2.45 MeV neutrons are indeed generated in the electrodes by reaction (vi). These γ-rays are generated by reaction (vii). We note that the intensities of the spectra are weak and, in agreement with this, the neutron flux calculated from measurements with the dosimeter is of the order 4×10^4 s^{-1} for a 0.4 cm × 10 cm rod electrode polarised at 64 mA cm^{-2}.

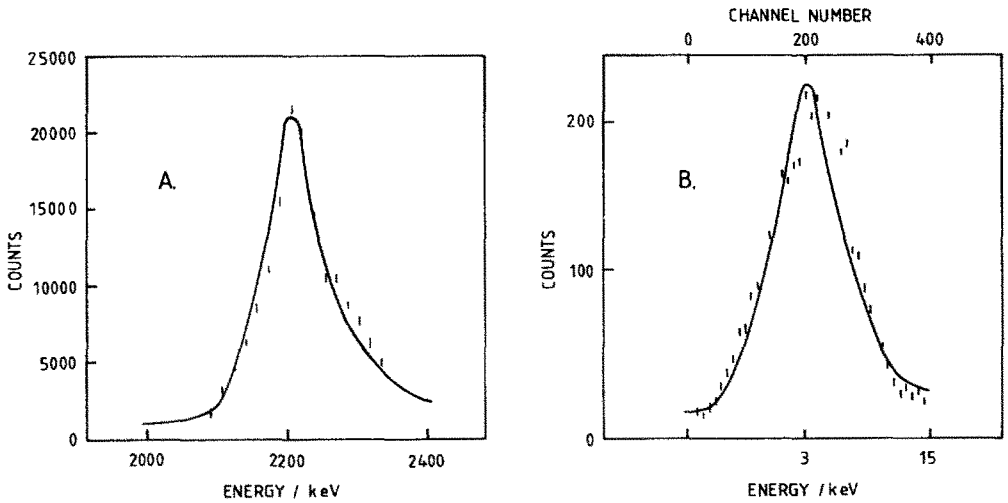

Fig. 1. (A) γ-ray spectrum recorded above the water bath containing the rod cathodes. Measurements carried out with a sodium iodide crystal scintillation detector and a Nuclear Data ND-6 High Energy Spectrum Analyzer. The spectrum shown is the difference between that over the water bath and a sink 5 m from the experiment containing identical shielding materials; spectrum accumulation times: 48 h. (B) β-ray disintegration scintillation spectrum measured with a Beckman LS5000TD counter-spectrometer.

Experiment (4)

In agreement with this low neutron flux, the accumulation in the electrolyte also indicates a low rate for reaction (v) [which has been found to be somewhat faster than (vi) in high energy physics experiments]. The time dependent fraction of tritium in the solvent can be shown to follow [5]

$$\alpha_T = \gamma_T \exp\frac{-(1+\lambda S_{D,T})Rt}{\gamma S_{D,T} N} + [(1+\lambda)\gamma_T + \beta / R] \times \frac{S_{D,T}}{(1+\lambda S_{D,T})}\left[1 - \exp\frac{-(1+\lambda S_{D,T})Rt}{\lambda S_{D,T} N}\right] \quad (1)$$

where γ_T is the fraction of T in the electrolyte/solvent feeds, λR (atoms T s^{-1}, here 4×10^{11} atoms s^{-1}) is the sampling rate which has been assumed to be continuous in time, N is the total number of atoms of D in the Dewar (14.6×10^{23}), $S_{D,T}$ is the D/T separation factor, β is the rate of the nuclear reaction (v) (events s^{-1}) and R is the rate of electrolysis expressed as atoms D s-1 (here 1.24×10^{18} atoms s^{-1}). It can be seen that the final value of α_T for the cell containing the Pt cathode (for which we assume $\beta_A = 0$) is

$$\alpha_T = [(1+\lambda)\gamma_T + \beta / R]\frac{S_{D,T}}{(1+\lambda S_{D,T})} \quad (2)$$

Blank experiments using Pt cathodes (which have very similar separation factors to Pd) indicate little accumulation of DTO so that $S_{D,T}$ is close to unity under the conditions of our experiments. DTO accumulates in the cells containing Pd cathodes to the extent of about 100 dpm ml^{-1} of electrolyte, and Fig. 1B demonstrates that the species accumulated is indeed tritium. Use of eqn. (2) then indicates that reaction (v) takes place to the extent of 1-2 $\times 10^4$ atoms s^{-1} which is consistent with the measurements of the neutron flux, bearing in mind the difference in radii. On the other hand, the data on enthalpy generation would require rates for reactions (v) and (vi) in the range 10^{11} - 10^{14} atoms s^{-1}. It is evident that reactions (v) and (vi) are only a small part of the overall reaction scheme and that other nuclear processes must be involved.

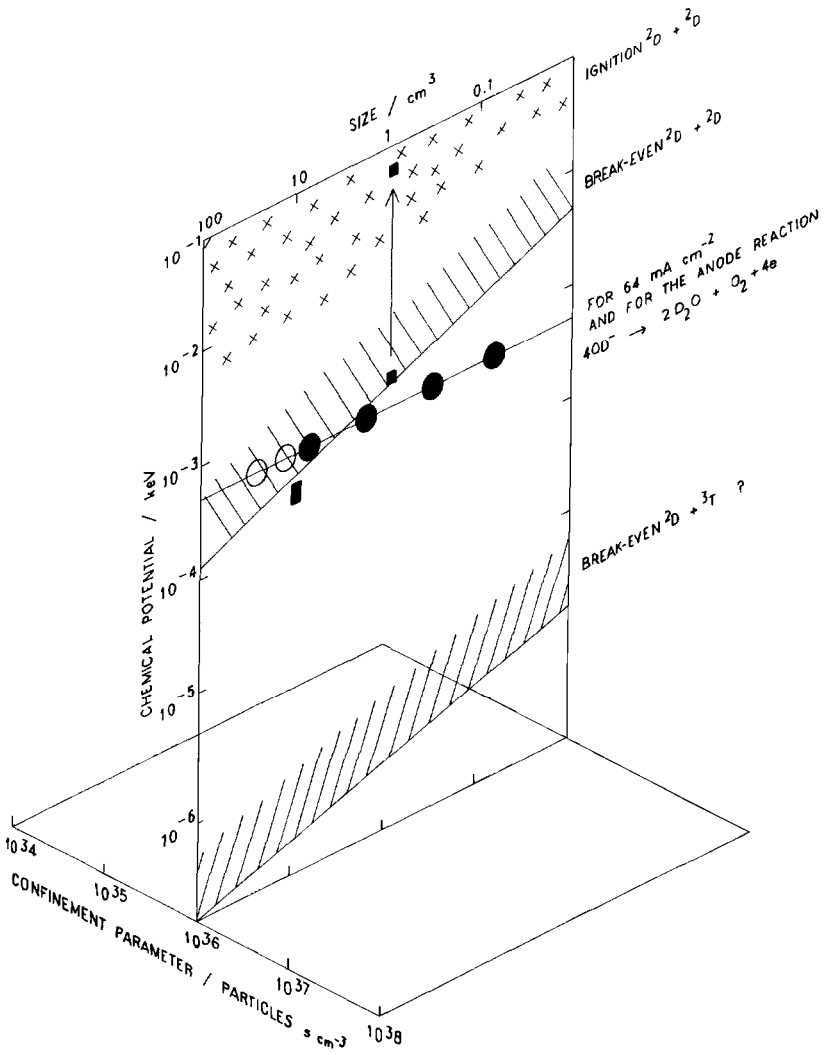

Fig. 2. Confinement parameter-chemical potential-size diagram for $^2D+ ^2D$ fusion reaction in Pd cathodes; projection to the $^2D+^3T$ reaction. Open circles: systems currently being investigated.

DISCUSSION

We realise that the results reported here raise more questions than they provide answers, and that much further work is required on this topic. The observation of the generation of neutrons and of tritium from electrochemically compressed D^+ in a Pd cathode is in itself a very surprising result and, evidently, it is necessary to reconsider the quantum mechanics of electrons and deuterons in such host lattices. In particular we must ask: is it possible to achieve a fusion rate of 10^{-19} s^{-1} for reactions (v) and (vi) for clusters of deuterons (presumably located in the octahedral lattice positions) at typical energies of 1 eV? Experiments on isotopically substituted hydrides of well defined structures might well answer this question.

The most surprising feature of our results however, is that reactions (v) and (vi) are only a small part of the overall reaction scheme and that the bulk of the energy release is due to an hitherto unknown nuclear process or processes (presumably again due to deuterons). We draw attention again to the very large magnitude of the effects in the confinement parameter diagram, Fig. 2. We note that the values of the confinement parameter are extremely high compared to conventional research on fusion (high particle densities, lifetimes of 10^5 - 10^6 years) while the chemical potential is very low compared to the equivalent parameter (*T*) in those experiments. It is evident that diagrams of this kind require extension in the third dimension for electrochemical experiments, since the results are so markedly

dependent on electrode volume (increase of current density displaces the points in a vertical direction). We draw attention again to the fact that the experiments already carried out are close to the break-even point; further work to extend the electrode dimensions (and to establish the nature of the processes responsible for the enthalpy release) is in progress. Finally, we urge the use of extreme caution in such experiments: a plausible interpretation of the experiment using the Pd-cube electrode is in terms of ignition. Projection of the values in Tables 1 and 2 to more extreme conditions indicates that this may indeed be feasible.

ACKNOWLEDGEMENT

We thank Johnson Matthey PLC for the loan of precious metals for this project.

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5 M. Fleischmann, M. Hawkins and S. Pons, J. Electroanal. Chem., to be submitted.

Errata

M. Fleischmann, S. Pons and M. Hawkins, Electrochemically Induced Nuclear Fusion of Deuterium. *J. Electroanal Chem.*, 261 (1989) 301-308

p. 301 (1) M. Fleischmann and S. Pons regret the inadvertent omission of the name of their co-author, Marvin Hawkins, Department of Chemistry, University of Utah, from the list of authors.

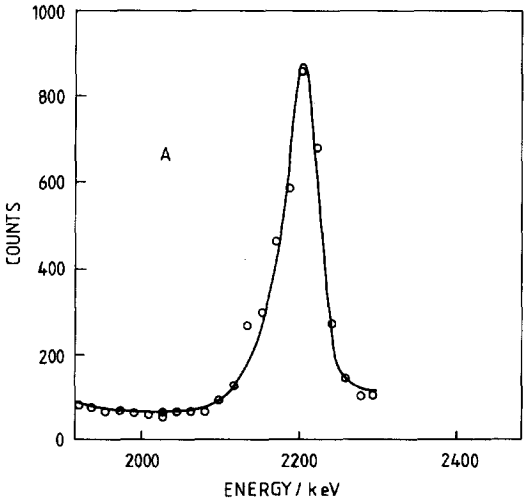
p. 302 (2) Line 23: 300 K should be 303.15 K.
(3) Last line: $^{1}H + n = {}^{2}D + \gamma(2.225\ MeV)$ (vii)

p. 303 (4) Line: "... equilibrium; background spectra over a water bath (containing identical shielding materials) 5 m from the water bath (48 h accumulation) were flat and < 400 counts."
(5) Line 15: omit "cosmic ray."
(6) $4\ OD^- = 2\ D_2O + O_2 + 4\ e^-$ (viii)

p. 304 (7) Table 1, column 3: There should be an arrow pointing from 250 to 125.

p. 305 (8) Table 2, last column 286 should be 143; 1224 should be 308.
(9) Last paragraph "...and this spectrum confirms that neutrons are indeed generated in the electrodes. These, γ-rays are generated by reaction (vi). We note that..."

p. 306 (10) Fig. IA: The y-axis should be labelled from 0 counts (minimum) to 1000 counts (maximum), ie. replace 0, 5000, 10000, 15000, 20000, and 25000 counts by 0, 200, 400, 600, 800, and 1000 counts respectively (as shown here).



(11) Fig. IA legend: "...Analyzer. The background in this region (taken for 48 h over a water bath 5 m from the experiment containing identical shielding materials) was level at = 400 counts (see text); spectrum accumulation time; 10 h..."
End of legend, add: Initial count rate 41 dpm; steady-state count rate 141 dpm.
(12) Text line 6: "...accumulation of tritium in the electrolyte..."

p. 307 (13) Line 6: 100 should be 50 - 100.
(14) Fig. 2 legend add: ● = rod, ■ = cube, and ▌sheet electrodes.

p. 308 (15) Line 20-21 "...(presumably again due to clusters of deuterons)..."