

AN OVERVIEW OF COLD FUSION PHENOMENA

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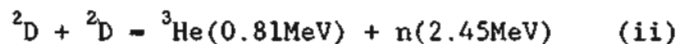
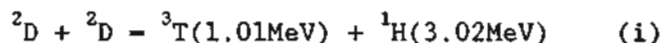
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Abstract

The present position of research in the field of Cold Fusion has already been outlined in two papers presented at this meeting.^(1,2) This report will therefore emphasize the early work and general considerations which led us to investigate the possibility of inducing nuclear reactions of D^+ in palladium electrodes⁽³⁾ (for some corrections see⁽⁴⁾); this is followed by a brief assessment of the position reached at the end of the first year of research in this field as summarized by the papers presented at this conference.

Historical Background

The discovery of the two major nuclear reaction paths of D^+



was reported by Oliphant, Harteck and Lord Rutherford in 1934 in a brief letter to Nature⁽⁵⁾; the precise values of the energy terms in reactions (i) and (ii) were established by subsequent research. This early work relied on the bombardment of perdeutero inorganic compounds such as $(ND_4)_2SO_4$ by deuterons of intermediate energies (~ 20 keV). The origins of this discovery have been largely forgotten presumably because deuterium and the deuteron were called diplogen and the diplon at that time. This neglect of the early literature is doubly unfortunate because the precise characterization of

reaction (i) using cloud chamber methods already showed at that time that a significant number of the tracks of the 3T and 1H species emerged at ~ 180°^(6,7)! To quote Philip Dee⁽⁷⁾: "this no doubt being the result of transmutations effected by slower diplons which have lost energy by collision in the target."

We believe that these reports are the first indication that there are low energy fusion channels in solid lattices.¹ The bombardment of heavy ice by deuterons of intermediate energy was used subsequently as a relatively intense source of neutrons⁽⁹⁾ but the neutron generating processes do not appear to have been further characterized. There have, however, sometimes been other indications that low energy deuterons undergo fusion reactions e.g., the production of neutrons from high density low ion temperature plasmas induced by electron cyclotron resonance heating in magnetic mirror devices.⁽¹⁰⁾

General Consideration of the Behavior of D^+ in Palladium Cathodes

We have already drawn attention^(3,11) to the strange behavior of D^+ electrochemically compressed into palladium cathodes.^(12,13) Fig. 1 illustrates a number of the important

¹Recent work on "warm fusion" induced in perdeuterated inorganic and organic materials by relatively low energy heavy water clusters⁽⁸⁾ may well be related to these early observations.

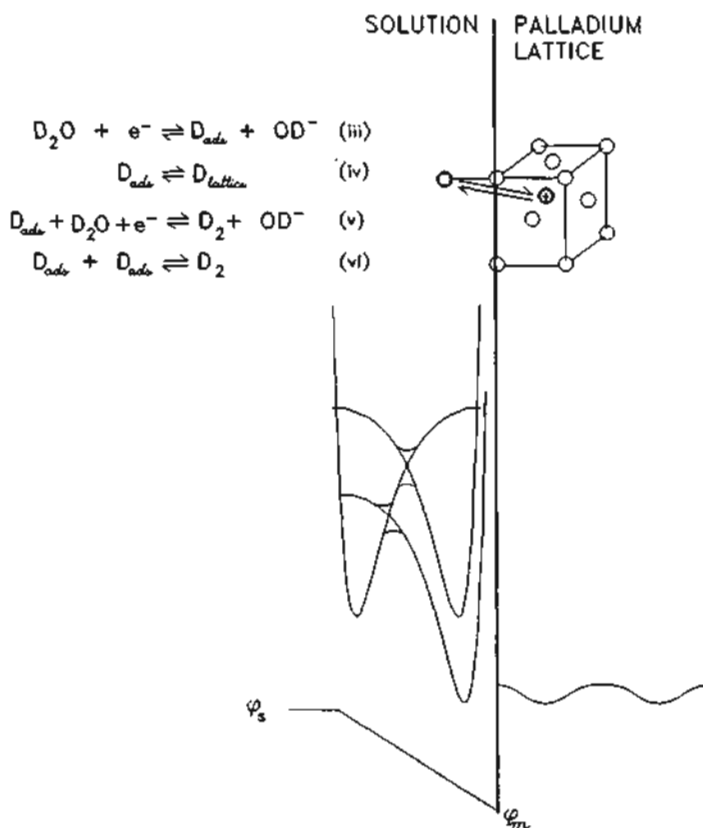


Figure 1. Schematic of the energetics in the solution, at the interface, and in the bulk of a palladium electrode during the electrolysis of heavy water containing LiOD, and a list of the pertinent reactions.

features of the discharge of D_2O and of D_2 evolution for electrolyses in alkaline media as well as of the dissolution of adsorbed D in the palladium lattice. At the reversible potential the initial state of reaction (iii) (a D_2O molecule interacting with its surroundings together with an electron in the Pd lattice) is in equilibrium with the final state (an adsorbed atom and a deuterioxide ion again interacting with their surroundings). For experiments close to atmospheric pressure the lattice is already in the β Pd-D phase. Increases in the difference of the galvanic potential between the metal and the solution $|\Delta(\phi_m - \phi_s)|$ (shown here in a highly simplified form as a linear drop in potential across the Helmholtz double layer) from the value at the reversible potential stabilize the final state with respect to the initial state to an extent $\Delta(\phi_m - \phi_s)F$ joules mole⁻¹. The adsorbed atoms are therefore "driven" onto the surface and, in turn, the adsorbed species

are "driven" into the FCC lattice, step (iv) where they exist as D^+ ions, almost certainly in the octahedral positions. The adsorbed species are desorbed in the further step (v). At very negative potentials, the D^+ species behave as classical oscillators.⁽¹⁵⁾

The concentration of D^+ in the lattice under equilibrium conditions is already very high ($D/Pd \approx 0.6 - 0.7$). The composition of the lattice at high negative potentials is still a subject of debate but it would be surprising if the D/Pd ratio did not approach or even exceed unity under these conditions (see results presented at this meeting).⁽¹⁴⁾ The dominant effect of the increase in cathodic potential must, however, be an increase in the activity of the dissolved deuterium. The activity will be determined under steady state conditions by the rates of steps (iii), (v) and (vi) but we will restrict attention here to a quasi-thermodynamic argument based on an hypothetical equilibrium of reactions (iii) and (iv). For such an equilibrium

we can equate the electrochemical potentials of the initial and final states

$$\bar{\mu}_{D,m}^+ + \bar{\mu}_{OD,s}^- = \mu_{D_2O,s} \quad (1)$$

or

$$\mu_{D,m}^+ + \phi_m F + \mu_{OD,s}^- - \phi_s F = \mu_{D_2O,s} \quad (2)$$

i.e.

$$\mu_{D,m}^+ = \mu_{D_2O,s} + \mu_{OD,s}^- - (\phi_m - \phi_s)F \quad (3)$$

In this expression $\mu_{D_2O,s}$ and $\mu_{OD,s}^-$ will be close to the standard state values. It should be noted that $\mu_{D,m}^+$, $\mu_{OD,s}^-$ and $(\phi_m - \phi_s)$ are quantities which are not accessible to thermodynamic measurement but the change in the chemical potential of the dissolved D^+ , $\Delta\mu_{D,m}^+$, due to a change in the galvanic potential difference $\Delta(\phi_m - \phi_s)$, from the value existing at the reversible potential is thermodynamically defined (as is $\Delta(\phi_m - \phi_s)$).

Values of $\Delta(\phi_m - \phi_s)$ as high as 0.8V can be achieved using conventional electrochemical systems and values even higher (in excess of 2V) could be achieved under special conditions.⁽¹⁵⁾ While the energy values $\Delta(\phi_m - \phi_s)F$ may appear to be modest, they are, in fact, of astronomical magnitude. Thus, if one were to attempt to achieve the same activity of dissolved D^+ by the compression of D_2 using steps (iv) and (vi) under equilibrium conditions (as is customary in heterogeneous catalysis) we would need to satisfy the condition

$$2\mu_{D,m}^+ + 2\mu_{e,m} = \mu_{D_2,g}^{\ominus} + RT \ln P_{D_2} \quad (4)$$

where P_{D_2} is the fugacity of the gaseous D_2 . We obtain

$$\mu_{D,m}^+ = \mu_{D_2,g}^{\ominus} / 2 - \mu_{e,m} + RT/2 \ln P_{D_2} \quad (5)$$

and, it can be seen that a 0.8 eV shift of the potential of the electrode corresponds to a $\approx 10^{27}$ fugacity of D_2 :

$$0.8F = RT/2 \ln P_{D_2} \quad (6)$$

Such high hydrostatic pressures are naturally not achievable on earth and, even if they were, other phenomena would intervene such as the formation of metallic D and collapse of the host lattice. The argument set out above is instructive, however, from several points of view: in the first place it points to the importance of the "poisoning" of the desorption steps (v) and (vi) so as to drive (iii) as close to equilibrium as is possible; secondly, it points to the special role of cathodic polarization in causing the "compression" of D^+ into the lattice; thirdly, it suggests that clusters of D^+ must form in the lattice under such extreme conditions by analogy to the nucleation of metals. Our interest in nucleation phenomena and our knowledge of the prediction of the formation of metallic hydrogen (and deuterium) at extreme compressions in United States and Soviet work during the mid 70's (e.g., see⁽¹⁶⁾) was, in fact, a key element in the initiation of this research project. The clustering of D^+ would be initiated at special sites or, possibly, at octahedral sites which would distort so that these sites would then be more correctly described as being parts of dislocation loops.

There were (and are) a number of further factors which point to the possibility of inducing nuclear reactions of electrochemically compressed deuterium. The dissolved D^+ is, in fact, a very high density, low ion temperature plasma existing in an high electron concentration. We can therefore pose the following conundrum: it would be expected that the s-electron density around the nuclei would be high but this would lead to the formation of D_2 . As this is not observed, the s-electron density must in fact be low. While we do not subscribe to the notion of the formation of heavy electrons, we recognize that the electron density in the clusters must be highly asymmetric and that it is necessary to develop a priori calculations about the many-body problem (taking into account the presence of the lattice) before it is possible to make any predictions of the Coulomb repulsion and nuclear motion in the clusters in the host

lattice² as well as the stability of the D⁺ species. Such calculations must also provide answers to other conundra such as why the diffusion coefficient of D in Pd/D exceeds those of both H in Pd/H and T in Pd/T.⁽¹⁷⁾ We recognize that some⁽¹⁸⁾ (many?) regard the principle of asymptotic freedom as sacrosanct and, therefore, that nuclear reactions of D⁺ could not be affected by many-body phenomena (coherent processes) in the lattice environment. This point of view is adhered to notwithstanding the fact that it is an approximation which may, or may not, hold in the limit of short space-times, the principle being increasingly called into question for other reasons, e.g.⁽¹⁹⁻²¹⁾. We, for our part, would not have started this investigation⁽³⁾ if we had accepted the view that nuclear reactions in host lattices could not be affected by coherent processes.

The background to this research has been presented from the point of view of the behavior of D⁺ in palladium cathodes since this has been our exclusive concern. A somewhat different account would be relevant to the behavior of deuterium in titanium, the other system which has been the subject of intensive research following the description of the generation of low levels of neutrons during cathodic polarization.⁽²²⁾

Assessment of the Present Position

Part of our early work leading up to our first publication⁽³⁾ was based on the search for evidence for reactions (i) and (ii) of D⁺ compressed electrochemically into palladium electrodes. To our great surprise we found that excess enthalpy was generated in the cathodes, the magnitude of this excess enthalpy increasing markedly with increase of the current density; levels of 10-20 watts cm⁻³ of the cathode material were reached at 512mA cm⁻². The most surprising aspect of the results was that although low levels of tritium and possibly neutron generation

could be detected, these levels were far too low to account for the generation of excess enthalpy. There appeared to be a rough equivalence of the rates of tritium and neutron generation at electrodes generating excess enthalpy above 1 watt cm⁻³. Neutron generation appeared to take place in "bursts."⁽²³⁾ Subsequent work has shown that there are also "bursts" in the excess enthalpy production superposed on the essentially steady state excess enthalpy production reached at long times.⁽²⁴⁾ Tritium production⁽²⁵⁾ also appears to take place in "bursts."⁽²⁵⁾

The work reported at this meeting (as well as in a number of publications and numerous announcements during the past year) supports most of the first findings.^(3,24) Steady state excess enthalpy production and "bursts" in enthalpy have been detected using a variety of calorimeters and calorimetric techniques (e.g., see the papers presented at this meeting). Rates of excess enthalpy generation above 100 watt cm⁻³ have been reached at 1A cm⁻³^(26,27) and these are sustained for times such that the total excess enthalpy is in the range 100-1000MJ cm⁻³⁽²⁶⁾; "bursts" in enthalpy as high as -16 MJ cm⁻³ have been observed.^(26,28) Such excess enthalpy generation clearly cannot be attributed to any chemical process(es).⁽³⁰⁾ Much higher levels of tritium generation (e.g., see^(25,31-33)) than those observed in the original work⁽³⁾ have now been reported and, as has been noted above, tritium generation also appears to take place in "bursts." The much more detailed and careful measurements of neutron production⁽³⁴⁾ than those in the original report⁽³⁾ indicate that this process takes place at a very low steady state level and in "bursts." This appears to be equally true for the Ti-D system where further measurements have been largely confined to gas loading experiments.⁽³⁵⁾ For the Pd-D system it is becoming apparent that the branching ratio for reactions (i) and (ii) differs markedly from the expected value of ~ 1^(31,32). While this report has concentrated on the work presented at this meeting, we also draw attention to the interesting work on neutron generation induced by gas phase discharges in palladium⁽³⁶⁾ rods saturated with deuterium.

New results reported at this meeting include the detection of soft

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²This was the background to our statement⁽³⁾ that it is necessary to reexamine the quantum mechanics of D⁺ and electrons in such host lattices.

X-rays^(31,37) (presumably by some type of coulomb excitation), of γ -rays⁽³⁸⁾ and the generation of charged particles following ion-implantation into Ti targets.^(31,39) As electrochemists we have found the measurements of the low frequency impedance of Pd cathodes at high overpotentials⁽³⁸⁾ of special interest. The inductive A.C. loop could well be due to the nucleation and growth of a new metallic phase (see above-metallic D?). The theoretical investigations⁽⁴⁰⁻⁴⁴⁾ have reached some degree of concensus in attributing Cold Fusion to the operation of coherent phenomena be they phonon or photon coupled or related to bound or unbound states. Experimentally testable predictions can be based on some of these theories (e.g., of tritium versus heat generation⁽⁴¹⁾).

While some of the more recent investigations indicate some degree of parallelism of the various phenomena (e.g. of tritium and neutron production and "bursts" in enthalpy^(32,45)) it is not yet by any means clear whether we are dealing with bulk or surface processes or both of these and whether and how all the disparate phenomena listed in Table 1 may be linked. The investigation of this aspect must clearly have high priority. It is now also essential to broaden the base of the research to include both the quantitative evaluation of the effects of

the many variables leading to the control and optimization of particular outputs (compare⁽⁴⁶⁾) and the extension of the range of systems showing the various effects. For the Pd-D system the central conundrum, the disparity of the excess enthalpy generation and of the expected nuclear products according to reactions (i) and (ii) however remains unsolved. It is clear that there must be other nuclear reaction paths of high cross-section and that these will only be discovered by a careful search for products on the surface and in the bulk of the electrodes (as well as in the solution and gas spaces). Experiments of this type will require electrode preparation under very clean conditions and analyses using XPS, Auger and high mass resolution SIMS measurements⁽⁴⁷⁾ as well as other high resolution mass spectroscopy. We arrive at the final conundrum: such experiments are essential to complete the description of the processes and are rightly requested.⁽⁴⁸⁾ However, while these experiments are certainly feasible they cannot be initiated, let alone completed, with present day funding levels and funding policies.

Conclusion

It is hardly possible that the

Excess enthalpy
 Bursts in enthalpy
 Tritium
 Bursts in tritium
 Neutrons
 Bursts in Neutrons
 X-rays
 Bursts in x-rays
 γ -rays
 Bursts in γ -rays
 Reaction products

Bulk,
 Surface,
 Special
 sites

Theory: coherent phenomena

Table I. The various phenomena which have been reported so far in the course of this research.

repeated observation of such a wide range of disparate phenomena can be explained away by the operation of a whole set of different systematic errors nor that we have been attending a seance of true believers.

References

- [1] G. H. Miley: this meeting.
 [2] D. Worledge: this meeting.
 [3] M. Fleischmann, S. Pons, and M. Hawkins, J. Electroanal Chem. 261 (1989).
 [4] M. Fleischmann, S. Pons, and M. Hawkins, J. Electroanal Chem. 263(1989) 187.
 [5] M. L. Oliphant, P. Harteck, and Lord Rutherford, Nature 133 (1934) 413.
 [6] P. I. Dee, Nature 133 (1934) 564.
 [7] P. I. Dee, Proc. Roy. Soc. A 148 (1935) 623.
 [8] R.J. Beuhler, G. Friedlander and L. Friedman, Phys. Rev. Lett., 63 (1989) 1292.
 [9] E.C. Pollard and W.L. Davidson, "Applied Nuclear Physics," John Wiley and Sons, New York, 1942.
 [10] W.B. Ard, M.L. Becker, R.A. Dandl, H.O. Eason, A.C. England and R.J. Kerr, Phys. Rev. Lett., 10 (1963) 87.
 [11] M. Fleischmann and S. Pons, Proceedings of the Joint N.S.F. - E.P.R.I. Meeting, Washington, D.C., November, 1989.
 [12] F. A. Lewis, "The Palladium Hydrogen System, Academic press, London, 1967.
 [13] B. Dandapani and M. Fleischmann, J. Electroanal. Chem. 39 (1972) 323.
 [14] R. Adzic, D. Gervasio, I. Bae, B. Cahan and E.B. Yeager: this meeting.
 [15] M. Fleischmann and S. Pons, to be published.
 [16] See the Rand Corporation Reports.
 [17] J. Vöelkl and G. Alefeld, Eds., "Hydrogen and Metals", vol. 2, in "Topics in Applied Physics", vol. 29, Springer Verlag, Berlin, (1978), chapter 12.
 [18] D. Lindley, Nature, 344 (1990) 375. Dr. Lindley does not phrase his comments in this way but this is what he implies.
 [19] G. Preparata, Phys. Rev., A38 (1988) 233.
 [20] E. Del Giudice, G. Preparata and G. Vitiello, Phys. Rev. Lett., 61 (1988)1085.
 [21] G. Preparata, "Quantum Field Theory of Superradiance" in "Problems of Fundamental Modern Physics," R. Cherubini, P. Dal Piaz and B. Minetti, Eds., World Scientific Press (1990).
 [22] S. Jones, E. Palmer, J. Czior, D. Decker, G. Jensen, J. Thorne, S. Taylor and J. Rafelski, Nature 338 (1989) 737.
 [23] This has been repeatedly reported in lectures given by us subsequent to our first announcement.
 [24] First reported by S. Pons at the 175th Meeting of the Electrochemical Society, Los Angeles, CA, May (1989).
 [25] N. J. C. Packham, K. L. Wolf, J. C. Wass, R. C. Kainthla, and J. O'M. Bockris, J. Electroanal. Chem. 270(1989) 451.
 [26] S. Pons: this meeting.
 [27] R. A. Oriani, J. C. Nelson, S. K. Lee, and J. H. Broadhurst, 176th Meeting of the Electrochemical Society, Hollywood, FL USA October (1989), and submitted to Nature.
 [28] M. Fleischmann, S. Pons, M. Anderson, L. J. Li, and M. Hawkins, J. Electroanal. Chem., in the press.
 [29] S. Pons and M. Fleischmann, J. Fusion Technology, in the press.
 [30] R. C. Kainthla, M. Sklarczyk, L. Kaba, G. H. Lin, O. Velev, N. J. C. Packham, J. C. Wass and J. O'M. Bockris, Inst. J. Hydrogen Energy 14 (1989) 771.
 [31] P.K. Iyengar and M. Srinivasan: this meeting.
 [32] J. O'M. Bockris, G.H. Liu and N.J.C. Packham: this meeting.
 [33] E. Storms and C. Talcott: this meeting.
 [34] M. Srinivasan, A. Shyam, S.B. Degwekar and L.V. Kulkavui: this meeting.
 [35] H.O. Menlove: this meeting.
 [36] N. Wada and K. Nishizawa, Japanese J. of Appl. Phys., 28(1989)665.
 [37] H. Bergerson: this meeting.
 [38] M.C.H. McKubre, R.C. Rocha-Filho, S. Smedley, F. Tanzella, B. Chexal, T. Passell and J. Santucci: this meeting.
 [39] G.C. Chambers, G. Hubler and K. Grabowski: this meeting.
 [40] J. Schwinger: this meeting.
 [41] G. Preparata: this meeting.
 [42] P.L. Hagelstein: this meeting.

- [43] S.R. Chubb and T.A. Chubb: this meeting.
- [44] R.T. Bush: this meeting.
- [45] C.D. Scott, J.E. Mrochek, M. Petek, T.C. Scott, G.E. Michaels and E. Newman: this meeting.
- [46] R.W. Bass: this meeting.
- [47] D.R. Rolison, W.E. O'Grady, R.J. Doyle, and P. P. Trzasko: this meeting.
- [48] Cold Fusion Research, A Report of the Energy Research Advisory Board to the United States Department of Energy, DOE/S-0073, November, 1989.