



Research Article

# Thermodynamic and Kinetic Observations Concerning the D + D Fusion Reaction for the Pd/D System

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## Abstract

Discussions with Professor Bockris prompted this thermodynamic and kinetic analysis of the D + D fusion reaction to form He-4. The results clearly show that this fusion reaction is thermodynamically possible at room temperatures. The kinetic analysis indicates that the reaction rate in the Pd/D system is controlled by the diffusion of deuterium within the palladium. Based on electrochemical double layer concepts, likely reaction zones exist near the surface of the palladium cathode.

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## 1. Introduction

The topics in this paper were based on my many correspondences with Professor John Bockris over several years prior to his death in 2013. The central topic was that Bockris believed his report of He-4 found in a palladium electrode [1] may have been due to mass spectrometry measurement errors. Bockris asked me for thermodynamic calculations for the D + D fusion reaction at 300 K and at  $10^8$  K because he believed that the production of He-4 by fusion reactions was perhaps not thermodynamically possible near room temperature. Also, knowing that I had been a student of Henry Eyring, Bockris asked what could be learned by applying the Eyring rate theory [2] to the D + D fusion reaction. My calculations, inspired by Bockris, are the main focus of this paper.

## 2. Thermodynamics

The main thermodynamic functions are the internal energy ( $U$ ), the enthalpy ( $H$ ), the entropy ( $S$ ), and the Gibbs energy ( $G$ ). The First Law of Thermodynamics is defined in terms of the heat ( $q$ ) and work ( $w$ ) where  $\Delta U = q + w$  [3]. Enthalpy is defined by  $H = U + PV$  and the Gibbs energy by  $G = U + PV - TS = H - TS$ , where  $P$ ,  $V$ , and  $T$  are the pressure, volume, and temperature, respectively [3]. The concept of entropy ( $S$ ) is introduced by the Second Law of Thermodynamics expressed by  $dS = dq/T$  for a reversible process [3]. The resulting criteria for a possible

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(spontaneous) reaction based on thermodynamics are that the change in the Gibbs energy ( $\Delta G$ ) must be negative for the conditions of constant temperature and pressure [3]. The change in enthalpy ( $\Delta H$ ) is not as useful because a negative value is required under conditions of constant entropy and pressure [3]. Laboratory conditions of constant  $T$  and  $P$  are readily attained while conditions for constant  $S$  and  $P$  would be much more difficult.

Thermodynamic values are needed for the D + D fusion reaction that produces He-4:



Assuming constant pressure,  $dH = dU + PdV$  and when only  $P$ - $V$  work is involved  $dU = dq - PdV$ , thus  $dH = dq$  or  $\Delta H = q_p$  where  $q_p$  is the heat at constant pressure. Therefore, for Eq. (1)

$$\Delta H = q_p = -23.846478 \times 10^6 \text{ eV.} \quad (2)$$

This value is determined using Einstein's equation,  $E = \Delta mc^2$ , where  $\Delta m$  is the change in mass for Eq. (1) [4]. The negative sign implies that this reaction (thermodynamic system) releases heat energy to the surroundings. Using  $1.60218 \times 10^{-19} \text{ J/eV}$  and  $6.02214 \times 10^{23}$  atoms per mol, yields  $\Delta H = -2.30084 \times 10^{12} \text{ J/mol}$  of He-4 produced at standard temperature (298.15 K) and pressure ( $10^5 \text{ Pa}$ ).

It is obvious that at constant temperature,  $\Delta G = \Delta H - T \Delta S$ . Therefore, we need  $\Delta S$  in order to determine  $\Delta G$  to see if D + D fusion (Reaction 1) is possible at room temperature. Although Eq. (1) is not a chemical reaction, the absolute entropy values ( $S^\circ$ ) for D ( $123.349 \text{ J mol}^{-1} \text{ K}^{-1}$ ) and He-4 ( $126.150 \text{ J mol}^{-1} \text{ K}^{-1}$ ) can be used to obtain  $\Delta S = -120.548 \text{ J mol}^{-1} \text{ K}^{-1}$  for this D + D fusion reaction. Because  $\Delta H \gg T \Delta S$ , we obtain  $\Delta G = -2.30084 \times 10^{12} \text{ J mol}^{-1}$  at 298.15 K. Thermodynamically, D + D fusion to form He-4 is clearly possible at room temperatures. However, thermodynamics can only address the initial and final states and provides no information about reaction rates, special conditions using palladium, or activation energies such as the coulomb barrier. The thermodynamic results will be the same whether D + D fusion occurs in the palladium lattice or elsewhere. Nevertheless, thermodynamics clearly states that D + D fusion is possible at room temperatures. There may be kinetic factors or special environments that control the reaction rate for D + D fusion, but thermodynamics is silent on such conditions.

The thermodynamic properties for the D + D fusion reaction (Eq. (1)) may be calculated at  $10^8 \text{ K}$  (as requested by Bockris) by the use of the heat capacities ( $C_p$ ) for He-4 and deuterium. These are both monatomic gases where  $C_p = 5R/2 = 20.786 \text{ J mol}^{-1} \text{ K}^{-1}$ , and this value is constant with temperature for monatomic gases [3]. Using

$$\Delta S(T_2) = \Delta S(T_1) + \Delta C_p \ln(T_2/T_1) \quad (3)$$

with  $\Delta C_p = -20.786 \text{ J mol}^{-1} \text{ K}^{-1}$  yields  $\Delta S = -385.010 \text{ J mol}^{-1} \text{ K}^{-1}$  at  $10^8 \text{ K}$ . The use of Kirchoff's law [3] yields  $\Delta H = -2.30292 \times 10^{12} \text{ J mol}^{-1}$  at  $10^8 \text{ K}$ . The application of  $\Delta G = \Delta H - T \Delta S$  gives  $\Delta G = -2.26442 \times 10^{12} \text{ J mol}^{-1}$  at  $10^8 \text{ K}$ . The results of these thermodynamic calculations are summarized in Table 1.

In summary, it cannot be stated that D + D fusion is impossible at room temperature based on thermodynamics. It can be said that the reaction rates are observed to be extremely slow due to the coulomb kinetic barrier. However, it can never be stated that there are absolutely no conditions where the reaction rate could become considerable faster at room temperature.

**Table 1.** Summary of thermodynamic values for D + D fusion to form He-4 at 298.15 K and at  $10^8 \text{ K}$ .

|   | 298.15 K                  | $10^8 \text{ K}$          |
|---|---------------------------|---------------------------|
| $\Delta H \text{ (J mol}^{-1}\text{)}$                | $-2.30084 \times 10^{12}$ | $-2.30292 \times 10^{12}$ |
| $\Delta S \text{ (J mol}^{-1} \text{ K}^{-1}\text{)}$ | -120.548                  | -385.010                  |
| $\Delta G \text{ (J mol}^{-1}\text{)}$                | $-2.30084 \times 10^{12}$ | $-2.26442 \times 10^{12}$ |

### 3. The Eyring Rate Theory Applied to D + D Fusion

The Eyring rate equation is generally applied to chemical reactions or physical processes such as diffusion where bonds between atoms are being broken and new bonds formed to give an activated complex. This is often called the transition-state theory for reaction rates [5]. However, the D + D fusion reaction in the Pd/D system may be controlled by chemical or physical processes where the Eyring equation could be applied. This Eyring equation expresses the rate constant as [2,3,5]

$$k = (k_B T/h) e^{-\Delta G^\ddagger/RT}, \quad (4)$$

where  $k_B$  is the Boltzmann constant ( $1.38065 \times 10^{-23} \text{ J K}^{-1}$ ),  $h$  the Planck constant ( $6.62607 \times 10^{-34} \text{ J s}$ ),  $T$  the Kelvin temperature,  $R$  the gas constant ( $8.31447 \text{ J K}^{-1} \text{ mol}^{-1}$ ) and  $\Delta G^\ddagger$  is the Gibbs activation energy ( $\text{J mol}^{-1}$ ). If we assume a typical cold fusion experimental excess power of 100 mW for a Pd cathode at 300 K, then the zero-order rate constant ( $k$ ) for D + D fusion to form He-4 would be  $2.6174 \times 10^{10}$  He-4 per second. For a given rate constant and temperature, Eq. (4) can be rearranged for the calculation of the Gibbs activation energy:

$$\Delta G^\ddagger = -RT \ln(kh/k_B T). \quad (5)$$

This calculation yields 13,700 J/mol or 0.142 eV at 300 K (1 eV = 96485 J mol<sup>-1</sup>). For the diffusion of deuterium atoms in palladium, the activation energy ( $E_A$ ) is reported as 0.206 eV between 218 and 333 K [6]. These two activation energy values for the D + D fusion reaction and D diffusion in palladium are surprisingly close. These values become even closer when the relationship,  $E_A = \Delta G^\ddagger + 2RT + T\Delta S^\ddagger$  is included that yields a calculated activation energy of 0.194 eV assuming that the entropy of activation,  $\Delta S^\ddagger$ , is zero. This suggests that the D + D fusion reaction in palladium may be controlled by the diffusion of D atoms into some fusion reaction zone. For comparisons, the activation energy ( $E_A$ ) for diffusion is reported as 0.23 eV for H in palladium between 230 and 760 K and as 0.276 eV for tritium in palladium between 290 and 323 K [6]. Using 0.206 eV (19.9 kJ mol<sup>-1</sup>) as the activation energy for D + D fusion in palladium, the excess power would double from 100 mW at 300 K to 200 mW at 329 K. This is approximately the temperature effect observed experimentally for excess power measurements in the Pd/D system for cold fusion experiments.

### 4. He-4 Measurements in Palladium Cathodes

Most helium measurements (He-3 and He-4) for palladium cathodes used in cold fusion experiments were performed by Brian Oliver, and these results are reported in a book by Hoffman [7]. The results for the Bockris (Texas A&M), samples are included. My analysis of Bockris results concluded that there was no significant He-4 production for samples 2 and 4. However, one measurement for sample 5 yielded  $50.4 \times 10^{12}$  atoms of He-4 per cm<sup>3</sup> of palladium compared to the mean of  $0.385 \times 10^{12}$  He-4/cm<sup>3</sup>. Brian Oliver claims that this could have been due to a “burp” from the instrument<sup>a</sup>, but this large He-4 result could have also been due to a localized D + D fusion reaction.

My analysis also showed high He-4 values for the Fleischmann–Pons rods from the University of Utah. For example, Rod #5 electrolyzed in D<sub>2</sub>O + LiOD gave a mean He-4 value of  $98.6 \times 10^{12}$  atoms/cm<sup>3</sup>. This value was significantly higher than the mean value of  $0.209 \times 10^{12}$  He-4/cm<sup>3</sup> for the “As Received” palladium Rod #2 from the University of Utah with no electrolysis. In contrast, my China Lake samples gave very low mean values of  $0.078 \times 10^{12}$  He-4/cm<sup>3</sup> or less. However, all China Lake samples were from Pd electrodes that had been polished and used again in a H<sub>2</sub>O control experiment prior to the analyses for He-4. The loading of the palladium with hydrogen and the subsequential deloading along with the surface polishing would likely have removed any helium present.

<sup>a</sup>B. Oliver, E-mail communication, 2013.

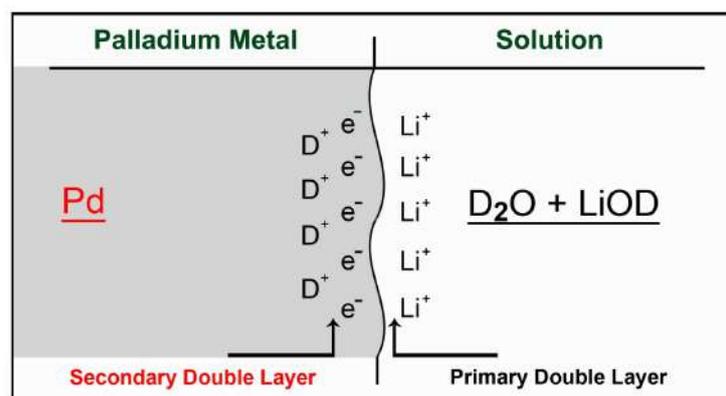
Furthermore, many of the China Lake samples were taken from the top of the cathodes where the palladium was covered by epoxy, hence no electrolysis occurred for those regions. These He-4 analyses destroyed the Johnson–Mattley rods that produced large excess heat effects at China Lake, and it took more than a year before other palladium samples were found that produced similar large effects. For a Pd/D electrode producing a typical excess power of  $1.0 \text{ W/cm}^3$  [8], then even Rod #5 from the University of Utah would require less than 7 min (377 s) to produce the reported  $98.6 \times 10^{12} \text{ He-4/cm}^3$ . This calculation is based on Eq. (1) that yields  $2.6174 \times 10^{11} \text{ He-4/s.W}$ . The much larger amounts of He-4 measured in the electrolysis gases [9] suggest that the fusion reaction must take place near the electrode surface where most of the helium is released from the palladium.

### 5. Possible Reaction Zones for D+ D Fusion in Palladium

If the rate of the D + D fusion reaction in the palladium system is controlled by the rate of diffusion of deuterium, then there must be active reaction sites or zones where this fusion is occurring. The diffusion of deuterium into these reaction zones is required for fusion. As an electrochemist, an interesting candidate for the active reaction zone is the electrochemical double layer at the palladium surface. For the Pd/D<sub>2</sub>O + LiOD system, this double layer would consist of excess electrons ( $e^-$ ) at the palladium cathode surface during electrolysis, and an opposing layer of excess lithium ions ( $\text{Li}^+$ ) in the adjacent solution. A typical potential change of 1.0 V across a double layer region of  $10^{-9} \text{ m}$  ( $10 \text{ \AA}$ ) yields an electric field strength of  $10^9 \text{ V m}^{-1}$  [10]. This electrochemical double layer acts as a capacitor with a typical capacitance of about  $20 \mu\text{F/cm}^2$  [10,11].

Palladium metal is unusual in that D can exist at high concentrations without forming D<sub>2</sub> in the lattice, and the diffusion rate of D is greater than either hydrogen or tritium [12]. Furthermore, D is present in palladium as the positive charged deuteron,  $\text{D}^+$  [12]. Therefore, a secondary double layer could be present near the palladium surface consisting of excess electrons at the surface and an opposing layer of deuterons ( $\text{D}^+$ ) just inside the palladium. A schematic representation of this is given in Fig. 1.

High palladium loading is required before a large concentration of  $\text{D}^+$  can exist in the secondary double layer. Otherwise,  $\text{D}^+$  will diffuse further into the bulk palladium due to concentration gradients. The D + D fusion reaction requires the diffusion of  $\text{D}^+$  (flux) across this secondary double layer zone. This can be in either directions as reported by McKubre [13]. Higher currents give a larger flux of deuterons across the reaction zone resulting in larger excess



**Figure 1.** Schematic representation of double layers as possible reaction zones for D + D fusion involving the palladium electrode.

heat measurements. The increase in excess heat with increasing temperature (positive feedback) is due to the increased rate of diffusion of deuterons at higher temperatures. It is possible that the long electrolysis time period before the excess heat effect is observed for palladium cathodes is due to the gradual buildup of silicates and other materials on the palladium surface. These substances block the palladium surface except for a few sites where there are very high current densities, large overpotentials, and much greater double layer effects. Such conditions are apparently needed for large excess heat effects. The large concentration of  $D^+$  in the palladium near the active electrochemical double layer sites are similar to the increase in  $D^+$  by electromigration in thin palladium wires to produce large excess heat effects as first proposed by Preparata [11,14].

## 6. Summary

My correspondences in recent years with Professor Bockris led to calculations on the thermodynamics and kinetics of the  $D + D$  fusion reaction to form He-4. Thermodynamics show that this fusion reaction is possible at room temperatures, but thermodynamics offers no information about the reaction rate. However, special conditions may exist where  $D + D$  fusion becomes considerable faster at room temperature as found in cold fusion experiments.

The application of the Eyring rate equation to the Pd/D system indicates that the  $D + D$  fusion reaction may be controlled by the diffusion rate of deuterium within the palladium. This suggests possible reaction zones for  $D + D$  fusion in palladium. These special zones may be double layer regions adjacent to the palladium cathode as well as inside the palladium but still near the surface.

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## Tribute to Professor Bockris

I was well aware of Professor Bockris' many contributions to electrochemistry long before the cold fusion controversy erupted in 1989. His support and publications on the cold fusion topic were very important in those early years because of his scientific reputation, and this attracted the wrath of critics both from within Texas A&M University and from outside troublemakers such as the so called science reporter, Gary Taubes. The early reports of tritium production by Bockris and co-workers helped many of us in obtaining financial support for our own research. Several important meetings were organized by Bockris at College Station in Texas. I remember attending two of these meetings. The first meeting I attended was held at the University on April 20, 1992 where Professor Takahashi of Japan was the special invited guest who presented his recent results showing large excess heat effects. The second meeting I attended a year or two later had to be held off campus because of the rancor against Bockris at Texas A&M University.

My many correspondences with Bockris were mainly in 2012 and 2013. I was surprised by the many Emails that I was receiving from Bockris early in 2013 following his 90th birthday on 5 January 2013. Even at this age, Bockris had strong opinions on various issues including He-4 measurements for cold fusion experiments. However, he maintained strong support for his experiments that produced tritium. I did not even know that he was ill until I received word that he had passed away on July 7, 2013 in Gainesville, Florida. I have missed receiving his many Emails. Professor Bockris will remain as one of the great pioneers who produced early evidence for cold fusion in the Pd/D system.

## References

- [1] C.C. Chein, D. Hodko, Z. Minevski and J.O'M. Bockris, On an electrode producing massive quantities of tritium and helium, *J. Electroanal. Chem.* **338** (1992) 189–212.
- [2] S. Glasstone, K.J. Laidler and H. Eyring, *The Theory of Rate Processes*, McGraw-Hill, NY, 1941, pp. 13–14, 575–577.
- [3] P. Atkins and J. de Paula, *Physical Chemistry*, 7th Edition, W.H. Freeman, NY, 2002, pp. 30–63, 90–115.
- [4] P.J. Mohr, B.N. Taylor and D.B. Newell, CODATA recommended values of the fundamental physical constants, 2010, *Rev. Mod. Phys.* **84** (2012) 1527–1605.
- [5] K.J. Laidler and M.C. King, The development of transition-state theory, *J. Phys. Chem.* **87** (1983) 2657–2664.
- [6] Y. Fukai, *The Metal–Hydrogen System: Basic Bulk Properties*, Springer-Verlag, Berlin, 1992, pp. 229–231.
- [7] N. Hoffman, A. Dialogue On Chemically Induced Nuclear Effects, American Nuclear Society, La Grange Park, Illinois, 1995, pp. 156–191.
- [8] M.H. Miles, B.F. Bush and D.E. Stilwell, Calorimetric principles and problems in measurements of excess power during Pd–D<sub>2</sub>O electrolysis, *J. Phys. Chem.* **98** (1994) 1948–1952.
- [9] M.H. Miles, Correlation of excess enthalpy and He-4 production: A Review in *Condensed Matter Nuclear Science*, P. Hagelstein and S. Chubb (Eds.), World Scientific, New Jersey, 2006, pp. 123–131.
- [10] P. Delahay, *Double Layer and Electrode Kinetics*, Interscience Publishers, NY, 1965, pp.41–44.
- [11] E. Del Giudice, A. DeNinno, M. Fleischmann, A. Frattolillo and G. Mengoli, Loading of H(D) in a Pd Lattice, in *The 9th Int. Conf. on Cold Fusion, Condensed Matter Nuclear Science*, Tsinghua University Press, Beijing, China, 2002, pp. 87–91.
- [12] M. Fleischmann, The present status of research in cold fusion in *The Science of Cold Fusion, Proc. of ICCF-2*, T. Bressani, E. Del Giudice, and G. Preparata (Eds.), Italian Physical Society, Bologna, Italy, 1991, pp. 475–487.
- [13] M.H. Miles and M.C.H. McKubre, Cold Fusion After a Quarter-Century: The Pd/D System in *Developments in Electrochemistry, Science ired by Martin Fleischmann*, D. Pletcher, Z.Q. Tian, and D.E. Williams (Eds.), Wiley, New York, Chapter 13, 2014, pp. 245–260.
- [14] G. Preparata, M. Scorletti and M. Verpelli, Isoperibolic calorimetry on modified Fleischmann–Pons cells, *J. Electroanal. Chem.* **411** (1996) 9–18.