



Obituary Note

## An Obituary note to John O'Mara Bockris (1923–2013)

T. Nejat Veziroglu\*

*President, International Association for Hydrogen Energy, Miami, FL, USA*

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**Abstract**

An Obituary note to John O'Mara Bockris.

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*Keywords:* Hydrogen association, Hydrogen economy, Hydrogen energy system, John Bockris, John O'Mara Bockris

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John O'Mara Bockris, a pioneer and proponent of the Hydrogen Energy System and Professor Emeritus of Texas A&M University, died on 7 July 2013 because of a heart complication in Gainesville, Florida, USA, at the age of 90. John was the first person to call the Hydrogen Energy System "Hydrogen Economy" in a paper entitled "The Hydrogen Economy: An Ultimate Economy?" co-authored with John Appleby and published in Environment This Month in 1972. I thought it was an excellent way of describing the Hydrogen Energy System, since energy is the locomotive of economy. Consequently, when I was planning the first international conference on hydrogen energy in 1973, I named it The Hydrogen Economy Miami Energy (THEME) Conference, which was held on 18–19 March 1974 in Miami Beach, Florida. I invited John and a few others working on hydrogen energy as invited lecturers to the conference. Personally, I met John for the first time at this conference. Although we had the same alma mater, the Imperial College London, and we were there at the same time in 1940s, we never met there, as John was studying Electrochemistry at the Royal College of Science and I was studying Mechanical Engineering at the City & Guilds College.

At the THEME Conference, together with nine other hydrogen energy enthusiasts and/or scientists (Hussein K. Abdel-Al of Egypt and Saudi Arabia, William J. D. Escher of USA, Cesare Marchetti of Italy and Austria, Anibal R. Martinez of Venezuela, Tokio Ohta of Japan, Walter Seifritz of Switzerland, William D. Van Vorst of USA, Kurt H. Weil of Germany and USA, and Robert M. Zweig of USA), John and I met at the Penthouse of the Playboy Plaza hotel in Miami Beach, where the THEME Conference was being held, on the evening of Monday, 18 March 1974. At the meeting, there was a passionate, yet deliberate debate. It was agreed that the Hydrogen Energy System was an idea whose time had arrived. It was the permanent solution to the depletion of fossil fuels. It was the permanent solution to the global environmental problems. Then, the discussion turned to whether there was a need for a formal organization.

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\*E-mail: [veziroglu@iahe.org](mailto:veziroglu@iahe.org)

John and Anibal (incidentally the one who took part in establishing the petroleum cartel OPEC) urged the founding of a society dedicated to crusade for the establishment of what seemed to be to the gathering, the inevitable and universal energy system, the Hydrogen Energy System. It was ironic that Anibal was proposing the establishment of an organization, which would make OPEC obsolete. As a result of the Penthouse meeting, the International Association for Hydrogen Energy (IAHE) was established by the end of the year 1974. All those who participated at the Penthouse meeting formed the first Board of Directors of IAHE, and I was elected the President.

After the THEME Conference, John and I became very close friends. We had the same aim, i.e., to establish the Hydrogen Economy throughout the World. We co-authored a book entitled “Solar Hydrogen Energy: The Power to Save the Earth”, and three papers, viz., “A Solar-Hydrogen Economy for USA”, “A Solar-Hydrogen Energy System for Environmental Capability”, and “Estimates of the Price of Hydrogen as a Medium for Wind and Solar Sources”. In 1986, John and I testified to the Energy and Environment Committee of the Congress in Washington, DC, about the advantages of the hydrogen energy system.

After working as an Assistant Professor at the Imperial College London, John joined the University of Pennsylvania, Philadelphia, as the Professor of Chemistry, 1953–1972. He then went on to the Flinders University of South Australia, as the Professor of Physical Science, 1972–1979. After that he joined the Texas A&M University as the Professor of Chemistry in 1979. He was promoted to the Distinguished Professor of Chemistry in 1980, and became Emeritus Professor in 1997.

John O’M. Bockris was one of the originators of the concept of the hydrogen energy system, and was a founder of the International Association for Hydrogen Energy (IAHE) in 1974. He served on the IAHE Board of Directors, was awarded the prestigious IAHE Jules Verne Award in 1998, and attained the Emeritus Board Director status in 2000. He has promoted awareness of Hydrogen Energy amongst the scientists, engineers and laymen through hundreds of publications and lecture presentations around the world. The hydrogen energy community mourns the loss of John O’M. Bockris. We offer our sincere condolences to his surviving family members and friends.



Obituary Note

## The Latest Environmental Contributions of John O'Mara Bockris

Solomon Zaromb<sup>\*,†</sup>

*Zaromb Research Corp., 9S 706 William Drive, Burr Ridge, IL 60527, USA*

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### Abstract

While widely acknowledged as the father of the Hydrogen Economy and worthy to be dubbed as grandfather of the Methanol Economy, John O'Mara Bockris (JOMB) continued to inspire important environmental advances to the end of his most creative life. His co-invention of what may turn out to be a ground-breaking US Patent 8,413,420 helps to open the way to capturing CO<sub>2</sub> from automotive exhausts and its conversion to recyclable methanol fuel, thereby greatly reducing and possibly even reversing global warming. Most recently, in a letter dated shortly before his death, published herein as the Appendix, JOMB pointed to inexpensive mass production of methanol from natural gas via the syngas route which may lead to the displacement of gasoline by methanol as the main automotive fuel and to major reductions in global CO<sub>2</sub> emissions.

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*Keywords:* Catalysts for methanol synthesis, Converting captured CO<sub>2</sub> to methanol, Methanol from natural gas, Methanol synthesis reactor, Syngas by steam reforming

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### 1. Introduction

Although Prof. John O'Mara Bockris, hereafter referred to as JOMB, has been widely recognized as the father of the Hydrogen Economy [1–3], he might also be dubbed as the grandfather of the Methanol Economy, having anticipated Nobelist George Olah [4] by some thirty years [5,6]. Their outstanding achievements in these fields through the first decade of this century are best summarized by JOMB [7] and Olah et al. [8].

JOMB's latest environmental contributions included co-invention with S. Zaromb of the recently issued US Patent 8,413,420 [9], which opens the way to the capture of CO<sub>2</sub> from motor vehicle exhausts and its conversion to methanol, possibly in repetitive cycles, thereby minimizing their atmospheric CO<sub>2</sub> imprint and thus slowing down or possibly even reversing global warming. As a follow-up to that invention, we reproduce in Appendix his letter of June 13, 2013, written shortly before his death, which inspired a further potential advance that is the focus of this paper.

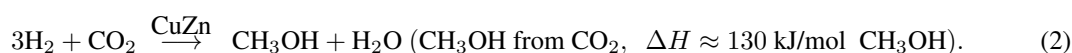
In the italicized portions of the Appendix, JOMB pointed out that:

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\*E-mail: zarombs@cs.com. Tel.: 1 630 654 2109; Fax: 1 630 986 8764.

†Retired, Argonne National Laboratory, Argonne, IL, USA.

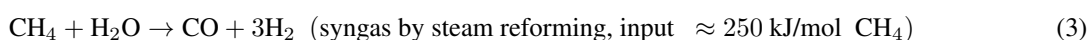
- (1) The recent and expected continued fall in natural gas prices opens the possibility of highly reduced costs of methanol production from steam-reformed natural gas via the reactions



- (2) As compared with the cost of 20–30 \$/GJ for the currently used electrolytic generation of the H<sub>2</sub> that is required by reaction (2), the costs entailed by reaction (1) should be less than 6 \$/GJ.  
 (3) Although reactions (1) and (2) would not result in any net removal of CO<sub>2</sub>, their implementation will yield a methanol fuel that will be more competitive than gasoline at current prices by a wide margin.

Indeed, JOMB's estimate of <6 \$/GJ for methanol from steam reformed gas translate to less than 0.9 \$/gallon, as compared with current methanol and gasoline prices of about 3 \$/gallon and 3.4 \$/gallon, respectively.

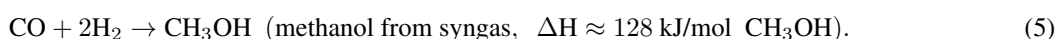
JOMB's "appropriate equation" results from steam reforming natural gas



followed by the water gas shift reaction [10,11]



Moreover, even more promising results are obtained with inclusion of the following key reaction:



Reactions (2), (3), and (5) can be combined in the ratio of 1:3:3 so as to yield substantially pure methanol



which implies no need of substantial electric power input to generate methanol from natural gas and captured CO<sub>2</sub> (vide infra). It also implies that captured CO<sub>2</sub> can also be converted to methanol in the same process without need of much additional electric power input.

The following section outlines some steps and modifications required for successful implementation of reactions (2), (3), and (5).

## 2. Methanol from Natural Gas and Carbon Dioxide

Of reactions (2), (3), and (5), only the steam reforming reaction (3) is endothermic, requiring a heat input of about 250 kJ/mol of CH<sub>4</sub>. That heat might be supplied by the exothermic reactions 2 [ $\Delta H \approx 130$  kJ/mol CH<sub>3</sub>OH] and 5 [ $\Delta H \approx 128$  kJ/mol CH<sub>3</sub>OH] by having all three reactions set to run together in an optimal ratio in a methanol synthesis reactor. This would result in up to a mole of captured CO<sub>2</sub> being used up per 4 mole of generated CH<sub>3</sub>OH.

Much of the vast amount of research on optimizing the catalysts and temperature cycling for the most practical utilization of the preceding reactions has been reviewed by Song and Pan [12] and more recently in a paper by Olah et al. [9], both of which teams caution about the care needed to avoid rapid deterioration of catalysts and point to the possibility of reactions (2), (3), and (5) being set to occur together. Moreover, Olah et al. [9] have arrived at reactant ratios similar to those of reaction (3) and (5) albeit by altogether different routes.

### 3. Conclusions

With the availability of large supplies of natural gas at reduced prices, the possibility arises of mass producing low cost methanol via the syngas route thereby displacing gasoline as the main automotive fuel and also reducing global warming by cleaner burning and by reduced costs of converting captured CO<sub>2</sub> to methanol.

This latest development inspired by JOMB's letter dated less than a month before his death may turn out, if put into practice, to be a crowning environmental contribution of his illustrious career.

### Appendix . JOMB'S Letter Dated June 18, 2013 [Unedited but with Parts in Italics]

John Bockris  
Haile Plantation  
10515 S.W. 55th Place  
Gainesville, FL 32608, USA  
E-mail: jbockris@cox.net  
Tel.: 352-335-3843; Fax: 352-335-6925  
June 18, 2013

Sol Zaromb  
E-mail: zarombs@cs.com

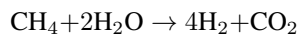
Dear Sol:

I have recently written to you about our possible patent not yet in our name and I have written as a helpful note to ask Mr. Langel to tell us what we might do to increase the legal status of my name in the patent. I know that the certificate of correction has been written although there is still the idea that I am supposed to write an added note to the certificate of correction which I have not done. (Should I do it, where should I send it, etc.?)

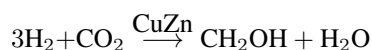
However, this note today is rather different, though not entirely unrelated, - suggestion which could be much worth a patent than what we have tried so far.

*I'm referring to the fact that natural gas prices have dropped by 25 percent in recent times and the findings are such that it's supposed to stay like that for at least twenty or thirty years. The supplies are enormous now and we should be exporting natural gas for many years.*

*Now, see what this means. If we steam reform natural gas, – a common reaction, the appropriate equation is:*



*Now, the formative equation for the desired methanol is:*



You will see then that what we produce from the natural gas steam reformed is pretty much what we need for synthesizing methanol. Yes, there would have to be a pressure change and a small amount of heat up to 300°C whereupon the reaction occurs, perhaps another 50°C might be helpful.

Now the point of the note to you is the cost of course. Made in the normal way whereby one could obtain the hydrogen from water by electrolysis of course goes up tremendously and three estimates I have made have costs between \$20 and \$30/GJ.

In respect to this suggestion, - that the desirable methanol should be made from natural gas, I have not had a professional estimate of its cost but as it comes from \$3/GJ natural gas, it can hardly be more than, say, \$6/GJ. This would look after the heating and the high pressure. Thus, when comparing \$6/GJ for our new methanol with \$25 for the one which got the hydrogen from water. Of course there is a penalty to be paid for this enormous attractive decrease in price and that is if we do it from CH<sub>4</sub>, we're not going to remove a molecule of CO<sub>2</sub> from the atmosphere when we make methanol and therefore it is not a global warming property.

On the other hand, as Olah has been stressing for many years, methanol in itself alone is a very worthy fuel and it was indeed suggested by me for the first time in 1975.

So now we're going back to creating methanol, – just methanol, – but its cost is only \$6/GJ.

Now can you convert \$/GJ to \$/Gallon. I think that if we go down by four times from \$25 to \$6, and as the methanol earlier was to cost \$4/GJ, the new methanol from natural gas would cost less than \$/Gallon!

Now, if I am right here, we certainly ought to make a patent because of course methanol is an extremely worthy fuel. Indeed Olah has been on this without any global warming properties for some years apart from my 1975 suggestion.

Please give this your own thought and whether my reasoning is reasonable and then we can consider what should be done about it!

I have always said that the only way to beat ExxonMobil will be to produce something cheaper than gasoline and that is what we have done here!

My best wishes.

Sincerely,

John O'M. Bockris

Distinguished Professor, Department of Chemistry

Texas A&M University, 1978–1997

Professor, Department of Chemistry, University of Pennsylvania, 1953–1972

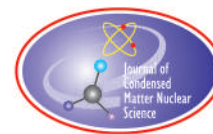
JOMB/ts

Zaromb 6/18/13 2

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Obituary Note

## In the Spirit of John Bockris

Edmund Storms\*

2140 Paseo Ponderosa, Santa Fe, NM 87501, USA

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### Abstract

The life of Prof. John Bockris provides a reminder of how good science should be undertaken and the harm a scientist and all of science suffer when these expectations are ignored.

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*Keywords:* Electrochemistry, John Bockris, Palladium, Transmutation, Tritium

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The spirit of Bernhardt Patrick John ÓMara Bockris left this world on July 7, 2013 after spending 90 years teaching us all how to be creative, mainly in electrochemistry, but most recently in cold fusion. He, along with Martin Fleischmann, provided our modern understanding of electrochemistry, for which he was rewarded with fame and admiration. If he had done nothing else, he would be remembered as an effective teacher, a good friend, and an example of the highest achievement in science.

But John went further by having the courage to study what is known as cold fusion. Thanks to his knowledge of electrochemistry and his friendship with Martin Fleischmann, who along with Stanley Pons [1], discovered the phenomenon, he was one of the first scientists to replicate the claim [2,3]. Normally, such success would have been considered a great achievement. Instead, certain professors at the University of Texas where he taught questioned his motives, honesty, and competence. This attack resulted in he and his wife being rejected by “friends”, an effort was made to strip him of his honor as Distinguished Professor, and the resulting legal problems required the services of a lawyer. The financial and emotional consequences took a toll on him and his family.

Meanwhile, Martin Fleischmann and Stanley Pons were experiencing similar irrational personal attack, requiring Martin to return to England and Stan to immigrate permanently to France with his family, where they were not subjected to such harsh treatment. While these three famous people provide examples of the most egregious irrational response to the discovery, almost every one who dared to study or advocate for the idea suffered. In addition to personal attack, certain powerful scientists created a myth by claiming the conclusions were not real, were an example of bad science, and were not worth the attention of anyone who valued their scientific career.

Over the next 25 years, the subject was largely hidden from the general public and conventional science. Major journals refused publication of papers, professors refused to encourage student interest, and financial support was denied by the effective policy of the DOE. Nevertheless, information about the unusual behavior accumulated until

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\*E-mail: storms2@ix.netcom.com



now the phenomenon has been proven real by overwhelming evidence. The skeptics and the small-minded attackers were proven wrong. Profs. Fleischmann and Pons have been vindicated. Only self-imposed ignorance now stops conventional science from accepting this fact.

You might wonder what this sorry tale has to do with John's life and death. John's life was devoted to teaching science at the highest level of competence and integrity. When he experienced the hostile treatment allowed by his university and the rejection by people he considered friends, he was naturally surprised, disappointed, and finally became angry. He spoke out in a paper describing the experience [4]. While his death stopped his ability to teach the proper way to have a scientific discussion, we the living have the responsibility to do the job. We all suffer the occasional consequence of ignorant and small minded behavior, but when a famous person of high standards and obvious competence, such as Profs. Bockris, Fleischmann, and Pons, are treated this way by the scientific society in general, a serious re-examination of scientific standards is required. Apparently, this process has to be undertaken in every field of science by every generation because the arrogance of the human mind is never cured, self-interest always trumps truth, and being smart does not make a person rational. Nevertheless, we all need to be reminded that new ideas must be considered with humility, objectivity, and knowledge, especially in the field of cold fusion itself.

Some new ideas are clearly wrong and need to be identified and improved. How this needs to be done is well understood in science. It does not and must not involve personal attack. Every kid who dreams of being a scientist knows this, so why is something so basic forgotten by some working scientists. Ideas must be evaluated by logic and knowledge. The rest of us need to keep reminding those scientists who forget how they are supposed to behave, as John would have wanted.

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Obituary Note

## Remembering John Bockris

Dennis Letts\*

*Lettslab, Austin, TX, USA*

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### Abstract

This brief note recalls the authors first interaction with Professor John Bockris in 1992 and how well Bockris could communicate lasting scientific truth.

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*Keywords:* Bockris, Cold fusion, Letts, RF, Triggering

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My initial contact with Dr. Bockris was a letter dated February 24, 1992 in which he commented on my idea for RF stimulation of Fleischmann–Pons electrochemical cells and provided many thought-provoking questions. There were also six items under the heading of “things to consider.” Item number 4 was “Dirty solutions work, not clean ones.”

This one comment stood out for some reason and I have kept it in mind for the last 22 years. Since 1992 I have built and tested more than 750 Fleischmann–Pons cells and the cells that worked have always been “dirty” with dark cathode surfaces. Over the years I have become known for laser stimulation methods and I must say that I have never observed laser-stimulated excess power from a shiny clean cathode.

Such was the genius of John Bockris – to make a prediction that would hold for more than two decades with just six words.

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\*E-mail: [lettslab@sbcbglobal.net](mailto:lettslab@sbcbglobal.net)



Obituary Note

## Personal Recollections of John O'Mara Bockris

Michael C.H. McKubre\*

*Energy Research Center, SRI International, CA, USA*

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### Abstract

Nobody contributed more to the development of physical electrochemistry than John Bockris. He did this directly through his thinking, research and teaching, and indirectly through his numerous publications and by taking responsibility for the training of the next generations of electrochemists in Europe, North America (twice) and Australia / New Zealand. My career might have been impossible, and would certainly have been greatly different, were it not for the direct and indirect contributions that John Bockris made to my life and learning. For this I am eternally grateful. Some details are described.

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*Keywords:* Graham Hills, John Bockris, John Tomlinson, Martin Fleischmann, Physical electrochemistry

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I first heard of John O'Mara Bockris in the Chemistry Department of Victoria University, Wellington, New Zealand, when I was finishing my bachelors degree. John Bockris' influence on the sub-discipline of physical electrochemistry was perhaps unequaled anywhere in the world – slightly less in the US – but the Bockris school of electrochemistry had a particularly strong influence in New Zealand. By the time I first met John in my masters year he was a living legend through his papers, books, and the stories told of him. He did not disappoint. Unlike the painfully uninteresting man in television advertising, John Bockris *was* the most interesting man in the world.

It is not possible to document fully the contributions that John Bockris made to the fields of electrochemistry, energy and science. He was the father of Physical Electrochemistry in which an attempt is made to understand the basic mechanistic processes that occur at a charged metal-electrolyte interface from a physical (rather than empirical) perspective. Such processes include all batteries and fuel cells, electrolysis, electro-synthesis, and corrosion, as well as many sensor and display applications. Our modern understanding of these phenomena owes more to John Bockris than to any other individual. Two other people might be mentioned in this context: Michael Faraday, the father of electrochemistry; and Alexander Frumkin who preceded slightly and pre-deceased John Bockris by many years. Frumkin fathered an exceedingly strong school of electrochemists in the then Soviet world. John was also a strong proponent of “the Hydrogen Economy” many decades before it was fashionable, and, in his later years, laid claim to the “first observation of a nuclear product in cold fusion experiments”. In his case this product was tritium and that

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\*E-mail: michael.mckubre@sri.com

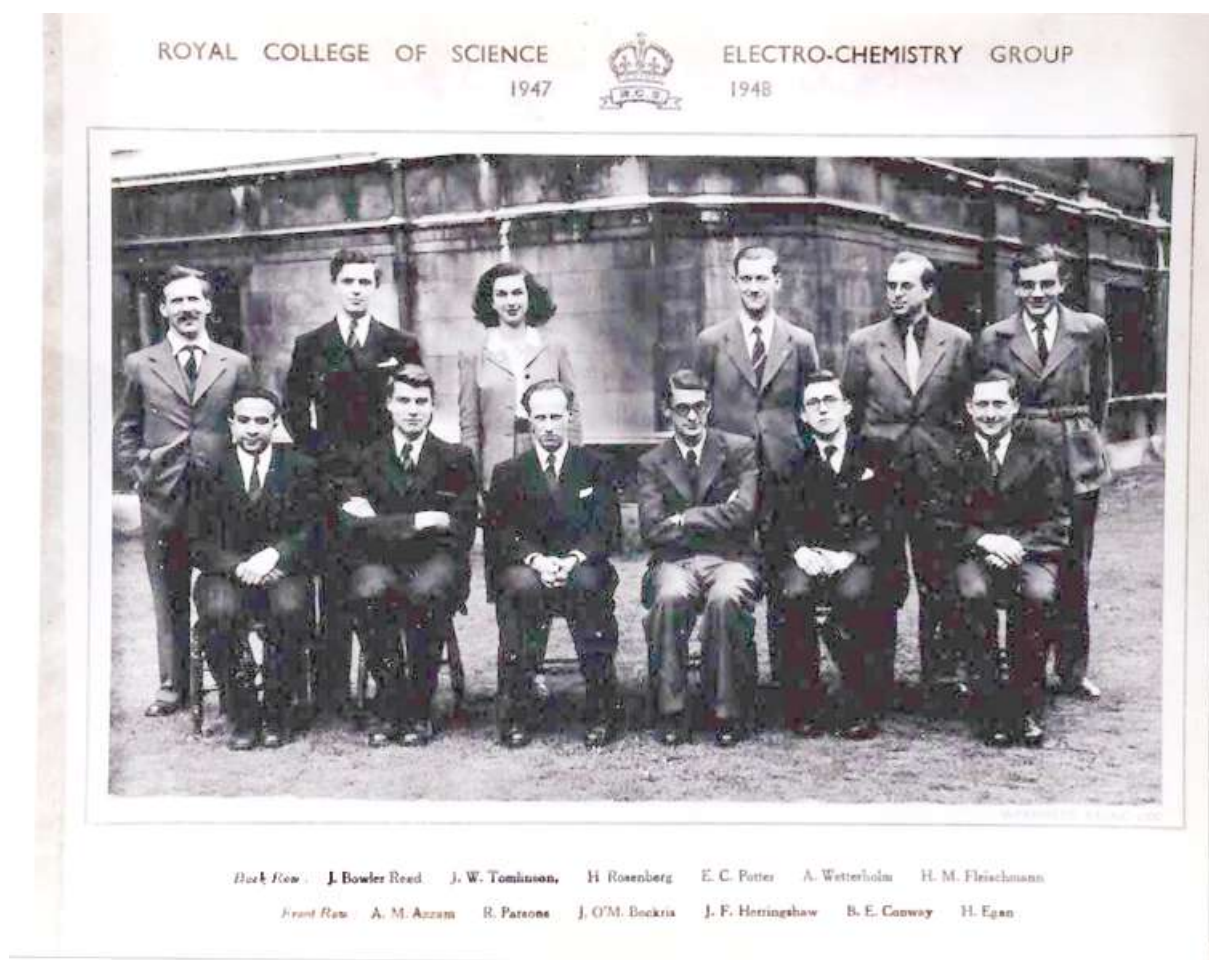
honor perhaps should be shared with Ed Storms and Carol Talcott, and with the BARC group headed by Srinivasan and Iyengar. But such was the stature of John Bockris that few would gainsay his claim.

Shortly after Martin Fleischmann died some of his friends put together a volume commemorating his contributions [1]. There were 19 chapters in all and could have been twice that length; each chapter was dedicated to a different aspect of Martin's creative output. Mel Miles and I contributed a chapter on Martin's last project, cold fusion. To my knowledge no such project has been contemplated or attempted for John Bockris, for two reasons I suspect. The great people that John Bockris created had largely pre-deceased him or long retired from influence. But the second reason is practical. Any comprehensive similar effort for John Bockris would extend to many hundreds of chapters that to some extent had already been accomplished in his lifetime. John was the driving force behind two highly influential series of books: *Modern Aspects in Electrochemistry*, edited initially with Brain Conway [2]; and *A Comprehensive Treatise* edited initially with Brain Conway and Earnest Yeager [3]. John is also survived and immortalized by the classic textbook of electrochemistry known affectionately and eponymously by the name of the authors: "Bockris and Reddy" [4]. First published in 1970 just at the time I was starting out, the textbook is taught today and is still relevant and insightful.

Rather than attempt the impossible I will confine myself to what I know, the effect that John Bockris had on me directly and indirectly in my formative years. The all-pervasive influence of John Bockris in electrochemistry in the English-speaking world had to be experienced to be appreciated. In the *Infinite Energy Obituary for John* [5] I stated that no man except my Father had more influence on me than John Bockris. I started writing this in Wellington, New Zealand, where I first met John Bockris, and first learned of his death some 42 years later. This influence, always positive, sometimes uniquely, occurred in several forms that I will attempt to remember and recount. I returned to NZ with my family after 4 years in the US, to Wellington where I was to continue my studies of physics and chemistry at Victoria University. Unlike the US, electrochemistry is taught in New Zealand at undergraduate level. With an inclination for the physical side of chemistry (and compensating disinclination for the organic side of chemistry) I naturally gravitated to electrochemistry. The first teaching texts I read on the subject and first research papers were written or co-written by John Bockris. This was not a coincidence although I did not appreciate that at the time. But my thinking about electrochemistry and the framing of the issues were conditioned by John Bockris and his immediate students from the time I first knew that electrochemistry and electrochemists existed.

At that point, 1969–1970, Victoria University of Wellington (affectionately known as "Vic") was undergoing something of a renaissance in physical and electrochemistry. The Professor of Physical Chemistry, my first John Bockris proxy, was John Tomlinson, one of Bockris' first group of Ph.D. students. John Tomlinson can be seen second from the left in the back row in Fig. 1, taken at Imperial College some time in 1947 or 1948. A few years earlier, in the middle of World War II, John Bockris had founded and built what was to become arguably the most influential and advanced school of electrochemistry the world has ever seen. It is said that "you are known by the company you keep". Professors are known by their writings and the students they produce. Few ever have matched John Bockris in either category. According to Wikipedia [6] Bockris authored and/or co-authored more than 712 papers and more than 24 books. About 250 people collaborated with Bockris between 1945 and 1997. Eighty-five students obtained a Ph.D. degree with his supervision. Many of these people are exceedingly eminent in their own right. Also seen in Fig. 1 are Roger Parsons, Brian Conway and Martin Fleischmann. Every one of these individuals was pivotal in creating the field of electrochemistry that we recognize today, and every one of them owes that stature to the teaching, training, mentoring and support provided by John Bockris.

Bockris was contacted when Victoria University of Wellington was looking for a Department Chair and Professor in Physical Chemistry. Bockris recommended John Tomlinson. He thought that Tomlinson would be a good fit for what was a prestigious appointment at one of New Zealand's top Universities, but still nevertheless somewhat of a scientific backwater. As with all (or most) Bockris' products, Tomlinson was brilliant. He displayed, however, a "cold British reserve" that many "Kiwis" found discomfiting and he was not aggressively ambitious. As a result Tomlinson



**Figure 1.** Bockris' Electrochemistry Group at Imperial College, 1947-1948.

had very few graduate students, and graduated only thirteen doctoral candidates in his sphere of influence over his 24 years at Victoria University [7]. In one of the first of many well-timed Bockris-inspired “coincidences” I applied to John Bockris’ hand picked man, John Tomlinson, to supervise my Masters and then Ph.D. degrees. It was just at that time that Bockris uprooted himself from the University of Pennsylvania where he had been for nearly two decades supervising one of the largest Electrochemistry groups in the world (see Fig. 2) that produced a significant fraction of the world’s more eminent electrochemists.

Bockris’ transition took place in 1971 with his chosen destination Flinders University in Adelaide, South Australia (see Fig. 3). Although 2000 miles (3200 km) of rough sea apart, Flinders is the closest major overseas university to Victoria. The strong personal bond between John Bockris and John Tomlinson meant that their two electrochemistry groups had strong overlap. Bockris visited often and, as Tomlinson’s Ph.D. student I dined occasionally with “John & John”, where my two seniors, almost like brothers, would regale their juniors with stories from “the dawn of science”, great men they knew and corresponded with, wine (of which both men were extremely knowledgeable and fond) and



**Figure 2.** Bockris' Electrochemistry Group at the University of Pennsylvania, 1953.

more mundane topics. Both men had exceedingly acute personal perception and finely honed senses of humor in the “British style”. Interestingly, although Bockris was born in South Africa and Fleischmann in what is now the Czech Republic, both men were exceedingly British in their manner and outlook. When he was in town Bockris attended chemistry department functions (traditionally “wine & cheese” parties with staff and students combined). I may be the only man in the field who has observed the great man, John Bockris, participate (enthusiastically) in a food fight.

In those days Bockris would give lectures, often *impromptu*, to the chemistry department at Vic. As I noted in my comments for Infinite Energy on the passing of John Bockris [5] “*On one occasion Professor Bockris gave the most impressive display of intellectuality I have ever witnessed. Conducting a lecture on no set topic to the mixed Chemistry Department, answering questions on any subject, he fielded perhaps a dozen questions in an hour or more, dealing with each thoroughly using direct quotations and complete citations written out on the blackboard — all from memory. I was exceedingly impressed and somewhat awed as I was about to go to Southampton for my postdoc (studying with another J. O’M. protégé — now Sir Graham Hills). I wondered — if they are all that good, how will I survive? They were not. There was only one John.*”

My trajectory to Southampton, and thus Martin Fleischmann, was also indirectly Bockris’ doing. When John left Imperial College London to try his hand in the new world colony of Pennsylvania he left behind his hand picked friend and colleague Graham Hills (later knighted to Sir Graham Hills) to look after his group and department at Imperial. Three years younger than John, Hills and Bockris were also extremely good friends. Graham deeply respected Bockris’ technical knowledge and people judgment. Hills maintained the stewardship of Bockris’ department at Imperial from 1953 to 1962 in which year he was appointed to Professor of Physical Chemistry at Southampton University on the



**Figure 3.** Bockris' third research group at Flinders University, 1975.

south coast of England (although I do not know this, almost certainly John Bockris' had assisted this appointment). With an industry of purpose and people management skill that I have never witnessed in another individual Hills set out to establish what turned out to be the next pre-eminent school of electrochemistry in the English speaking world. To do this Graham needed a leader. On the recommendation of John Bockris, Graham Hills selected Martin Fleischmann.

The reason to desire postdoctoral access to Southampton was the presence there of two giants and the institutional credibility established by them: Graham Hills and Martin Fleischmann; both intimately connected to John Bockris. But my opportunity at Southampton was forged at heavy price by others. Graham Hills' first wife Brenda died in 1974. To enable Graham to attend his wife during a long illness and be with their children afterwards, John Tomlinson spent most of a year in Southampton, operating in Graham's stead, in the department and the university. It was this created bond of respect and friendship that allowed Tomlinson to propose my name to Graham Hills when his fledgling student was looking for a postdoc at a "good school" in the "motherland".

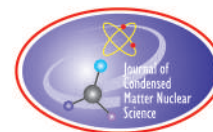
When my wife Carolyn and I arrived in Southampton on Christmas Day in 1976 Graham was waiting for us on the railway platform from London. Without having exhibited any reason to deserve it, this bond of respect and friendship was transferred without demand or condition to my wife and I, allowing me to establish myself in the chemistry department at Southampton, and hence to know Martin. Without having come to know personally, and respect intellectually Martin Fleischmann in those years (and Stan Pons, also), I doubt I would have taken seriously

the claims of March 1989 or taken serious effort to check out Fleischmann and Pons' proposition of nuclear effects in PdD. With such twists of fate careers are created and consumed. I would like to take this opportunity, sadly in all cases posthumously, of thanking the four giants of this tale without all of whom I would not be writing this story today: John O'Mara Bockris; John Tomlinson; Sir Graham Hills; Martin Fleischmann. All were extraordinary men in their own right. But none of these would have had the careers they had, nor made the contributions that they have made, without the first and greatest, John Bockris. And neither would I.

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Research Article

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

Melvin H. Miles\*

*Department of Chemistry, University of LaVerne, La Verne, CA 91750, USA*

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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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*Keywords:* Activation energy, Diffusion, Double layer, Eyring rate theory, Fusion reaction zones, Helium

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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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\*E-mail: melmiles1@juno.com

(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  $1.60218 \times 10^{-19}$  J/eV and  $6.02214 \times 10^{23}$  atoms per mol, yields  $\Delta H = -2.30084 \times 10^{12}$  J/mol of He-4 produced at standard temperature (298.15 K) and pressure ( $10^5$  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  $10^8$  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  $10^8$  K. The use of Kirchoff's law [3] yields  $\Delta H = -2.30292 \times 10^{12} \text{ J mol}^{-1}$  at  $10^8$  K. The application of  $\Delta G = \Delta H - T \Delta S$  gives  $\Delta G = -2.26442 \times 10^{12} \text{ J mol}^{-1}$  at  $10^8$  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  $10^8$  K.

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

### 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.

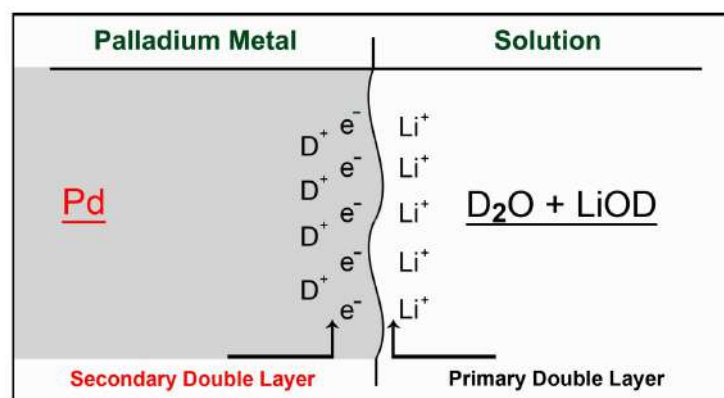
Furthermore, many of the China Lake samples were taken from the top of the cathodes where the palladium was covered by epoxy, hence no electrolysis occurred for those regions. These He-4 analyses destroyed the Johnson–Mattley rods that produced large excess heat effects at China Lake, and it took more 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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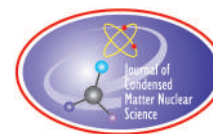
## Tribute to Professor Bockris

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.

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Research Article

# Equation of State and Fugacity Models for H<sub>2</sub> and for D<sub>2</sub>

Peter L. Hagelstein\*

*Massachusetts Institute of Technology, Cambridge, MA 02139, USA*

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**Abstract**

When Pd is in equilibrium with H<sub>2</sub> or D<sub>2</sub> in gas, the chemical potentials are equal, and this allows a determination of the chemical potential and other thermodynamic properties of palladium hydride and palladium deuteride. At high loading near room temperature, the gas pressure must be very high, and an ideal gas law no longer applies. In this case a knowledge of the fugacity is required to interpret and understand the results. We examine empirical models for the equation of state and fugacity of H<sub>2</sub> which are relevant to the high pressure regime of interest, including an old model of Holley et al (1958), and the more modern models of Spycher and Reed (1988), Tkacz and Litwiniuk (2002), and Joubert (2010). At high pressure the more recent models are best, but the model of Tkacz and Litwiniuk diverges from the ideal gas equation of state at low pressure, which leads to an offset in the fugacity. We examine the difference between the equation of states for H<sub>2</sub> and D<sub>2</sub> in recent models, and find that the small difference at high pressure in the models of Tkacz and Litwiniuk agree best with experiment, while the larger difference in the models of Joubert (2010) and Joubert and Thiebaut (2011) is probably not reliable. We examine the possibility of developing a difference correction for the fugacity theoretically. It may be possible to account accurately for the zero-point contribution; however, accounting for the difference in inter-molecular potentials due to the different degrees of rotational excitation requires the development of new potential models.

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*Keywords:* Equation of state, Fugacity, Gaseous H<sub>2</sub> and D<sub>2</sub>, Nonideal gas, Quantum cell model

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**1. Introduction**

In experiments where thermodynamic equilibrium is established between hydrogen in the gas phase and the metal hydride phase, by definition the hydrogen chemical potential is matched. Early in the last century the entropy of the ideal gas was established theoretically [1,2]; this provides a basis for the computation of the chemical potential, and allows for the determination of the chemical potential of hydrogen in Pd and other metals from pressure-composition-temperature experiments. The subsequent development of theoretical models for the chemical potential of hydrogen in metal hydrides followed [3].

For excess heat to be produced in the Fleischmann-Pons experiment [4,5] a very high deuterium loading in the Pd cathode is required [6]. We have been interested for some time in the development of models relevant to excess heat

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\*E-mail: plh@mit.edu

production, and from our perspective it would be of interest to model the deuterium loading in a manner consistent with the occupation of vacancies and other defects. Near room temperature the deuterium pressure that corresponds to the high D/Pd loading required is very high (near 1 GPa), sufficiently high that an ideal gas law model would not give very good results. In this regime in order to develop a relevant model for the chemical potential of deuterium in Pd in this regime, a knowledge of the equation of state of  $D_2$  is necessary. From the equation of state the fugacity of  $D_2$  can be determined [7], and with such a model it is possible to develop a model for the chemical potential of deuterium in Pd from experiments in which the loading is measured at high pressure.

Conceptually this seems straightforward. Ultimately a knowledge of the equation of state derives from experiment, so this motivates an interest in what experimental data is available. As might be expected, the equation of state of hydrogen and deuterium as a dense gas or liquid has been much studied over the years, and there are many data sets in relevant pressure and temperature regimes [8–16]. Considerable effort has also been put into the modeling of the equation of state as well, and one can find empirical models which are in good agreement with experiment [17–34]; some of the more recent of these focus on the temperature and pressure regime that we are interested in.

One might think that this should be the end of the story, but as could be expected there are a number of issues which have remain, and which have drawn our attention. For example, there is a recent empirical model by Tkacz and Litwiniuk [27] which has been widely used. If one compares predictions from this model to an older model favored by Bockris et al. [7], one finds significant differences at high pressure. Since the older model is based on the Beattie–Bridgeman empirical equation of state [35] (which dates from the 1920s), and fitted before 1960 by Holley et al. [19], when pressure–volume–temperature data was available for a much smaller range of pressures than in more modern times, one would expect that the more recent model should be preferred. Probably it would come as a surprise that near room temperature the older model is better, since there is a problem with the form of the fit employed by Tkacz and Litwiniuk [27]. Unfortunately the Tkacz and Litwiniuk model does not go to the ideal gas limit at low pressure.

Our attention is then drawn to the more recent empirical model by Joubert [31] for hydrogen, which looks to be the best available at this time for the parameter regime of interest. A very similar empirical model was put forth by Joubert and Thiebaut [32] for deuterium, which also looks to be very good. Of course, with such good models for hydrogen and for deuterium, the question naturally arises as to whether one might be able to address the relatively small and subtle differences between the fugacity of hydrogen and deuterium with these models reliably. Upon comparing the difference between the two models near room temperature at high pressure, our conclusion is that there is more difference than in experiment. Probably one cannot use these models then to study the relatively small difference between  $H_2$  and  $D_2$  and expect reliable results.

In what follows, we focus first on the equation of state of hydrogen, and then consider the associated fugacity. Subsequently we look at the difference between hydrogen and deuterium equation of state, and then consider the possibility of developing an estimate for the difference based on theory.

## 2. Equation of State Models for $H_2$

As discussed in Section 1, our understanding of the chemical potential of hydrogen in palladium hydride at high loading requires an understanding of the equation of state of gaseous and liquid hydrogen at high pressure. In connection with the discussion below, we recall the ideal gas law written as

$$PV = RT, \quad (1)$$

where  $P$  is the pressure,  $V$  the volume per mole,  $T$  the temperature and  $R$  is the gas constant. At high pressure where the equation of state is not ideal, we will be working with empirical gas laws which will specify a functional relation between the pressure, volume and temperature. As mentioned above there are many equation of state models in the



**Table 1.** Fitting parameters for the equation of state of H<sub>2</sub> based on the Beattie–Bridgeman equation from Ref. [19]; the pressure is in atmospheres, and the volume is in l/mol.

Parameter	Value
$A_0$	0.1975
$a$	−0.00506
$B_0$	0.02096
$b$	−0.04359
$c$	$5.04 \times 10^{-6}$
$R$	0.08206

literature for hydrogen and deuterium which are potentially of interest in our discussion [17–34]; however, only a few of these seem relevant over a range extending up to a few GPa near room temperature, which is the regime of interest to us in connection with the Fleischmann–Pons experiment. We will focus below on the four that seem most interesting.

### 2.1. Model of Holley et al. [19]

One of these is the Beattie–Bridgeman equation [35] of state, which we can write as

$$PV^2 = RT \left(1 - \frac{c}{VT^3}\right) \left(V + B_0 - \frac{bB_0}{V}\right) - A_0 \left(1 - \frac{a}{V}\right). \quad (2)$$

The five parameters of the model (listed in Table 1) were fit to PVT data for H<sub>2</sub> as reported by Holley et al. [19]. We were initially drawn to this model since it was referenced by Bockris et al. [7] in connection with the Fleischmann–Pons experiment.

### 2.2. Model of Spycher and Reed [23]

A more modern model in the form

$$\frac{PV}{RT} = 1 + \left(\frac{a}{T^2} + \frac{b}{T} + c\right)P + \left(\frac{d}{T^2} + \frac{e}{T} + g\right)P^2 \quad (3)$$

was published by Spycher and Reed [23]. The version of the model for hydrogen was fit to data up to 3000 bar, over a temperature range from 25 to 600°C. The parameters of the model are given in Table 2.

**Table 2.** Fitting parameters for the equation of state of H<sub>2</sub> based on the Spycher–Reed model [23]; the pressure is in bar.

Parameter	Value
$a$	−12.5908
$b$	0.259789
$c$	$-7.24730 \times 10^{-5}$
$d$	$4.71947 \times 10^{-3}$
$e$	$-2.69962 \times 10^{-5}$
$g$	$2.15622 \times 10^{-8}$

**Table 3.** Fitting parameters for the equation of state of H<sub>2</sub> based on the Tkacz and Litwiniuk model [27]; the pressure is in MPa, and the volume is in cm<sup>3</sup>/mol.

Parameter	Value
<i>A</i>	176.330
<i>B</i>	−633.675
<i>C</i>	−304.574
<i>D</i>	731.393
<i>E</i>	8.59805

### 2.3. Model of Tkacz and Litwiniuk [27]

The equation of state due to Tkacz and Litwiniuk [27] can be written as

$$V = \frac{A}{P^{1/3}} + \frac{B}{P^{2/3}} + \frac{C}{P^{4/3}} + \frac{D + ET}{P}, \quad (4)$$

where the fitting parameters were optimized taking into account recent high pressure measurements with diamond anvil cells. Model parameters appear in Table 3.

### 2.4. Model of Joubert [31]

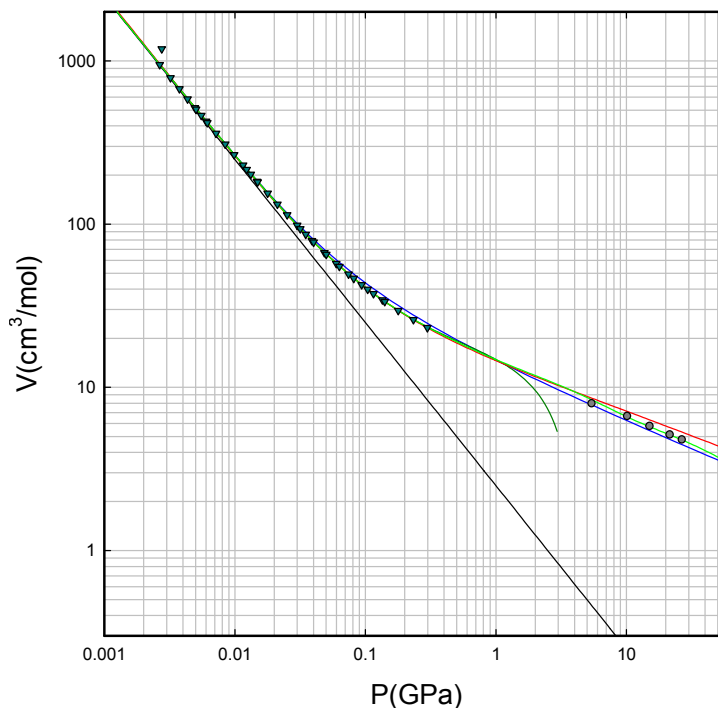
Our last equation of state is given by Joubert [31], and this one is given as

$$V = \frac{RT}{P} + a_1 e^{-P/b_1} + a_2 e^{-P/b_2} + a_3 e^{-P/b_3} + a_4 e^{-P/b_4} + a_5 e^{-P/b_5} + c. \quad (5)$$

This model was developed for use with the CALPHAD thermal physics software packages [36–38], and takes advantage of experimental *PVT* measurements up to high pressure. Fitting parameters are given in Table 4.

**Table 4.** Fitting parameters for the equation of state of H<sub>2</sub> based on the model of Joubert [31]; the pressure is in Pa, and the volume is in m<sup>3</sup>/mol.

Parameter	Value
<i>a</i> <sub>1</sub>	4.29 × 10 <sup>−6</sup>
<i>a</i> <sub>2</sub>	6.35 × 10 <sup>−6</sup>
<i>a</i> <sub>3</sub>	4.25 × 10 <sup>−6</sup>
<i>a</i> <sub>4</sub>	−1.50 × 10 <sup>−6</sup>
<i>a</i> <sub>5</sub>	−1.63 × 10 <sup>−6</sup>
<i>b</i> <sub>1</sub>	5.35 × 10 <sup>8</sup>
<i>b</i> <sub>2</sub>	4.21 × 10 <sup>9</sup>
<i>b</i> <sub>3</sub>	3.99 × 10 <sup>10</sup>
<i>b</i> <sub>4</sub>	2.90 × 10 <sup>7</sup>
<i>b</i> <sub>5</sub>	8.02 × 10 <sup>7</sup>
<i>c</i>	2.479 × 10 <sup>−6</sup>
<i>R</i>	8.31451



**Figure 1.** Results for  $V$  as a function of  $P$ ; ideal gas (black line); Beattie–Bridgeman model fitted by Holley et al. (blue line); Spycher and Reed model (dark green line); Tkacz and Litwiniuk model (red line); Joubert model (light green line); data of Hemley et al. [15] (gray circles); data of Michels et al. [8] (dark cyan triangles)

## 2.5. Volume as a function of pressure

We compare these models with experiment at room temperature in Fig. 1, where we plot the volume  $V$  as a function of pressure  $P$ . We show data points from the measurements of Michels et al. [8] as quoted in [27], and from the measurements of Hemley et al. [15]. We note that all of the models considered are in good agreement with the measurements of Mills et al. [9] between 0.2 and 2 GPa (not shown).

Perhaps the first thing to note is a substantial increase of the volume relative to the ideal gas law (the low black line), which is why we need an equation of state model to begin with. Next we note that the model of Spycher and Reed (1988) deviates from the other models above 1 GPa, which is due to our extending the model well out of range of the upper limit of pressures use for the fit (0.3 GPa). The other models are reasonably close to the experimental data, even at high pressure which might have been out of range for the Beattie-Bridgeman model.

We note that molecular hydrogen undergoes a phase change between the liquid phase and solid phase near 5.7 GPa at room temperature [11,39,40]. There is a volume change associated with this phase change [13], which is about  $0.3 \text{ cm}^3/\text{mol}$  at a volume of about  $8 \text{ cm}^3/\text{mol}$ . This volume change needs to be taken into account for high precision thermodynamics modeling. However, at this point we have no relevant data for PdH or PdD at such a high pressure, and the effect is small on the scale of our present considerations. We will ignore it in this work.

## 2.6. Discussion

We see a clear deviation of the equation of state above about 25 MPa from the ideal gas law in Fig. 1, which provides motivation for our interest in the fugacity.

Based on the discussion so far, we conclude that three of the equation of state models appear to give results in good agreement with experiment over the full range from atmospheric pressures up to the the highest data point shown at 26.5 GPa. The Beattie–Bridgeman fit is a bit high in the vicinity of 100 MPa, and the Tkacz-Litwiniuk model seems a bit high around 20 GPa. Nevertheless we are generally pleased, and we would expect that these models might reasonably be used for thermodynamic modeling near room temperature, specifically for the fugacity which we consider next.

## 3. Models for the Fugacity of H<sub>2</sub>

From the equation of state models considered in the previous section, it is possible to construct models for the fugacity by integrating. It will be useful here to review briefly what fugacity is in the context of extending the ideal gas chemical potential.

### 3.1. Ideal gas chemical potential and fugacity for a nonideal gas

It is possible to derive the entropy of an ideal gas from first principles, which leads to the Sackur–Tetrode entropy, which in a physics notation can be written as

$$S(N, E, v) = Nk_B \left\{ \frac{3}{2} \ln \left( \frac{E}{N} \right) - \ln \left( \frac{N}{v} \right) + \frac{3}{2} \ln \left( \frac{M}{3\pi\hbar^2} \right) + \frac{5}{2} \right\}. \quad (6)$$

Here  $N$  is the number of atoms or molecules,  $k_B$  Boltzmann's constant,  $E$  the energy,  $v$  the volume, and  $M$  is the mass. From this entropy model we can derive the chemical potential according to

$$-\frac{\mu}{T} = \left( \frac{\partial S}{\partial N} \right)_{E,v}. \quad (7)$$

The chemical potential in this model satisfies

$$-\frac{\mu}{k_B T} = \frac{3}{2} \ln \left( \frac{E}{N} \right) - \ln \left( \frac{N}{v} \right) + \frac{3}{2} \ln \left( \frac{M}{3\pi\hbar^2} \right). \quad (8)$$

The other partial derivatives of the Sackur–Tetrode relation lead to

$$\frac{E}{N} = \frac{3}{2} k_B T \quad (9)$$

and

$$Pv = Nk_B T. \quad (10)$$

We can make use of these relations at constant temperature to write the chemical potential in the form

$$\mu = \mu_0 + kT \ln \frac{P}{P_0}. \quad (11)$$

We see that the chemical potential at constant temperature is logarithmic in the pressure. It was noticed that a very similar formula could be used for the chemical potential at constant temperature in the case of a nonideal gas if one worked with the fugacity  $f$

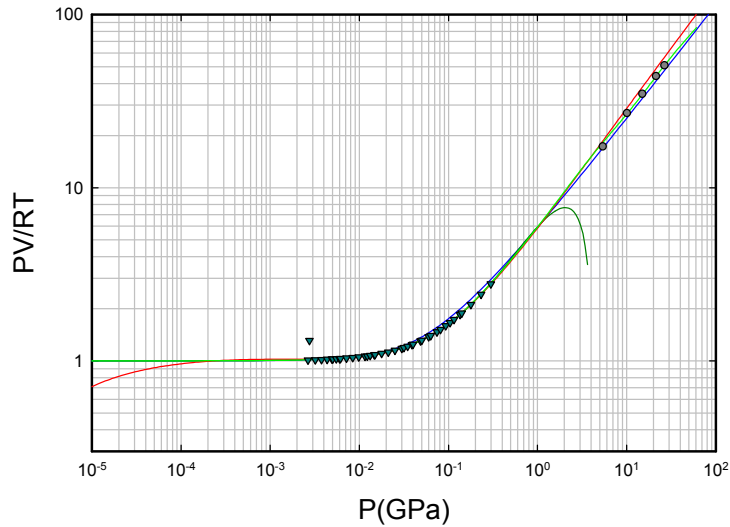
$$\mu = \mu_0 + kT \ln \frac{f}{f_0}, \quad (12)$$

where the fugacity satisfies

$$\ln \frac{f}{P} = \int_0^P \left( \frac{P'v}{Nk_B T} - 1 \right) \frac{dP'}{P'}. \quad (13)$$

It will be convenient to switch back to a chemistry notation to write this as

$$\ln \frac{f}{P} = \int_0^P \left( \frac{P'V}{RT} - 1 \right) \frac{dP'}{P'}. \quad (14)$$



**Figure 2.** Results for  $PV/RT$  as a function of  $P$ ; Beattie–Bridgeman model fitted by Holley et al. (blue line); Spycher and Reed model (dark green line); Tkacz and Litwiniuk model (red line); Joubert model (light green line); data of Hemley et al. [15] (gray circles); data of Michels et al. [8] (dark cyan triangles)

### 3.2. The compressibility factor

We see that the integral appearing in the computation of the fugacity involves the compressibility factor

$$z = \frac{PV}{RT}.$$

This motivates us to examine the compressibility for the different equation of state models considered in the previous section. Results are illustrated in Fig. 2 for the different models compared with experimental data. We notice that the compressibility factor increases at high pressure, which is where we would have expected deviations from the ideal gas law. As was the case previously we see that the model of Spycher and Reed [23] begins to deviate from the other models above 1 GPa.

### 3.3. Divergence of $PV/RT$ in the model of Tkacz and Litwiniuk

However, this time we notice that the model of Tkacz and Litwiniuk [27] starts dropping below unity at low pressure. We did not see it previously as our earlier plot did not extend down to sufficiently low pressure. The problem in this case is that the form used for the fit does not go to the ideal gas law as  $P \rightarrow 0$ . To illustrate this, we may write

$$\begin{aligned} \frac{PV}{RT} &= 1 + \frac{P}{RT} \left( \frac{A}{P^{1/3}} + \frac{B}{P^{2/3}} + \frac{C}{P^{4/3}} + \frac{D}{P} \right) \\ &= 1 + \frac{1}{RT} \left( AP^{2/3} + BP^{1/3} + \frac{C}{P^{1/3}} + D \right) \rightarrow \frac{1}{RT} \frac{C}{P^{1/3}}. \end{aligned} \quad (15)$$

The compressibility diverges at low pressure in this model. Unfortunately, this will lead to headaches later on.

### 3.4. Fugacity from the different models

A nice feature of the algebraic form for the different equation of state models we are interested in is that it is possible to carry out the integration required to compute the fugacity analytically. In the case of the Beattie–Bridgeman model, Holley et al. [19] give

$$\ln f = \ln \frac{RT}{V} + \frac{2}{V} \left( B_0 - \frac{c}{T^3} - \frac{A_0}{RT} \right) - \frac{3}{2V^2} \left( bB_0 + \frac{cB_0}{T^3} - \frac{aA_0}{RT} \right) + \frac{4}{3V^3} \frac{cbB_0}{T^3}. \quad (16)$$

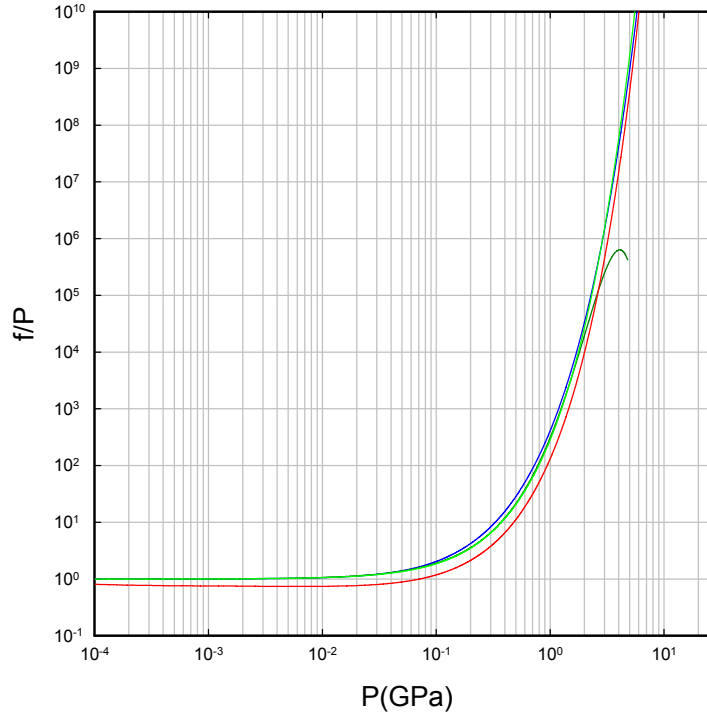
For the model of Spycher and Reed [23] we can write

$$\ln \frac{f}{P} = P \left( \frac{a}{T^2} + \frac{b}{T} + c \right) + \frac{P^2}{2} \left( \frac{d}{T^2} + \frac{e}{T} + g \right) \quad (17)$$

Tkacz and Litwiniuk [27] give

$$\ln f = \frac{1.5AP^{2/3} + 3BP^{1/3} + (D + ET) \ln P - 3CP^{-1/3}}{RT}. \quad (18)$$

Finally, we can carry out the integration for the model of Joubert [31] to obtain



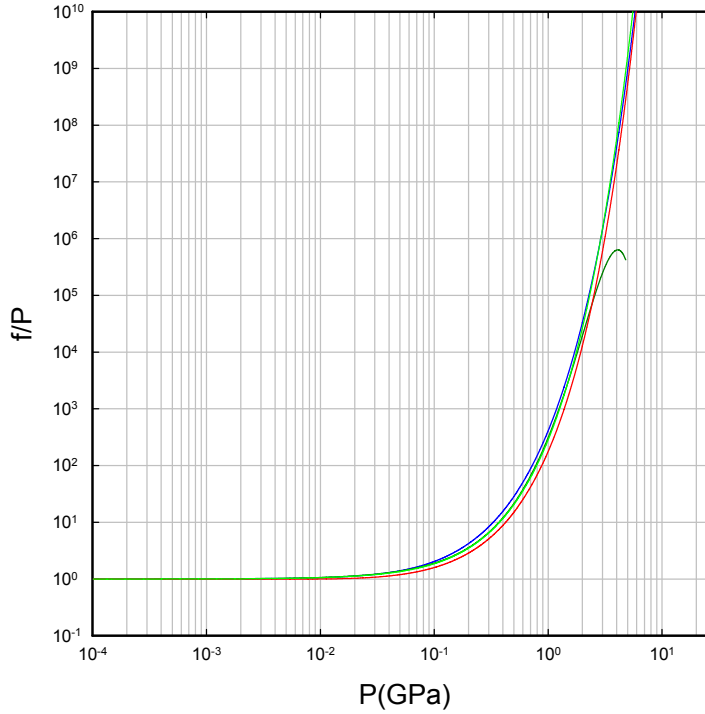
**Figure 3.** Results for the ratio  $f/P$  as a function of  $P$  at  $T = 300$  K; Beattie–Bridgeman model fitted by Holley et al. (blue line); Spycher and Reed model (dark green line); Tkacz and Litwiniuk model (red line); Joubert model (light green line)

$$\ln \frac{f}{P} = \frac{1}{RT} \left[ a_1 b_1 (1 - e^{-P/b_1}) + a_2 b_2 (1 - e^{-P/b_2}) + a_3 b_3 (1 - e^{-P/b_3}) \right. \\ \left. + a_4 b_4 (1 - e^{-P/b_4}) + a_5 b_5 (1 - e^{-P/b_5}) + cP \right] \quad (19)$$

Results for the ratio of fugacity to pressure at room temperature (300 K) are shown in Fig. 3. Broadly we see that the ratio increases strongly at high pressure, indicating that the deviations from the ideal gas law are significant above 100 MPa. The ratio based on the model of Spycher and Reed [23] begins to deviate from the results of the other models above a few GPa (which is out of range for the model). We notice that the ratio from the Tkacz and Litwiniuk model is low by a roughly constant offset at low pressure, which is a consequence of model deviating from the ideal gas law below 1 GPa.

### 3.5. Modification of the Tkacz and Litwiniuk model

We might develop a modification of the model of Tkacz and Litwiniuk in order to remove the low pressure problem. Perhaps the simplest modification is to set the compressibility ratio to unity whenever it goes below; for example we may write



**Figure 4.** Results for the ratio  $f/P$  as a function of  $P$  at  $T = 300$  K; Beattie–Bridgeman model fitted by Holley et al. (blue line); Spycher and Reed model (dark green line); modified Tkacz and Litwiniuk model (red line); Joubert model (light green line)

$$z' = \begin{cases} 1 & \text{for } z < 1, \\ z & \text{for } z > 1. \end{cases} \quad (20)$$

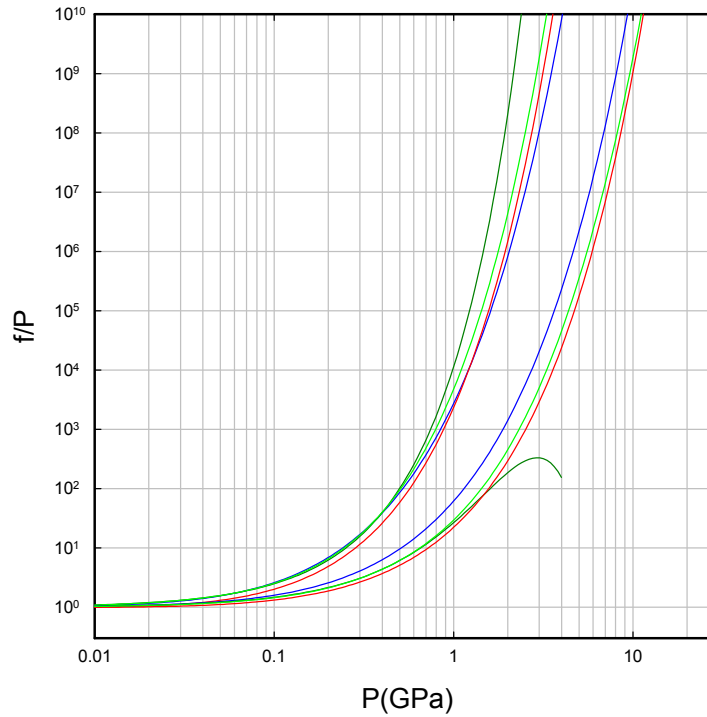
Results are shown in Fig. 4. We see that this modification generally reduces differences with the other models. Nevertheless, the modified version of the model remains noticeably low between 0.1 GPa and a few GPa.

### 3.6. Fugacity models at different temperatures

The Spycher and Reed model was fit using data between 25 and 600°C, while the Joubert model is based on data at both lower and higher temperature. The data sets available to Holley and coworkers was more limited, so we should expect poorer performance at other temperatures.

A comparison of the different models at 200 and at 500 K is shown in Fig. 5. Above about 0.5 GPa the Spycher and Reed model wanders away from the others; once again we note that this model is fit to data up to 0.3 GPa, and above 25°C, so much of the comparison here exercises the model outside of its range. The older Beattie–Bridgeman model fitted by Holley et al. is clearly the outlier away from room temperature of the remaining three. In general the modified Tkacz and Litwiniuk model tracks the Joubert model reasonably well at both temperatures. We see that the modified Tkacz and Litwiniuk model is a bit lower, similar to the case at 300 K.





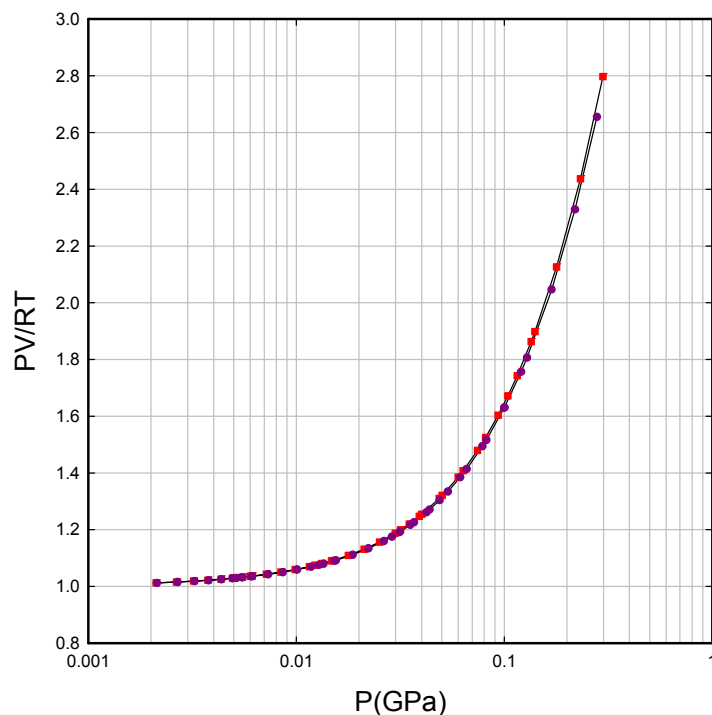
**Figure 5.** Results for  $f/P$  as a function of  $P$  at  $T = 200$  K (upper curves) and at  $T = 500$  K (lower curves); Beattie–Bridgeman model fitted by Holley et al. (blue line); Spycher and Reed model (dark green line); modified Tkacz and Litwiniuk model (red line); Joubert model (light green line)

### 3.7. Discussion

There are a number of observations that might be made based on this comparison. We were impressed by the older equation of state and fugacity of Holley et al. near room temperature, which does pretty well at pressures much higher than was available when it was constructed; however, we see that the resulting fugacity is not so good away from room temperature. The Spycher and Reed model looks good in the vicinity of the data used for its construction, but the fugacity is not so good when the equation of state is used out of range. The equation of state for the Tkacz and Litwiniuk model looks good except at low pressure where it deviates from the ideal gas law, and the corresponding fugacity is off at low pressure, and also low at higher pressures. The “new” equation of state and fugacity of Joubert is fitted over a wide range of temperatures and pressures, and doesn’t suffer from headaches at low pressure. It looks to be superior to all of the others considered in this work.

## 4. Difference between $D_2$ and $H_2$

We are interested in this section in the equation of state for  $D_2$  at high pressure, and in the difference between the equation of state and fugacity between  $D_2$  and  $H_2$ . Before focusing in detail, we note that we might expect the two equations of state to be very similar. So one of the issues before us is whether we might get good results using an  $H_2$  model



**Figure 6.** Compression ratio  $PV/RT$  for  $H_2$  (light red squares) and for  $D_2$  (dark pink circles) at  $25^\circ\text{C}$  as a function of pressure.

for the fugacity of  $D_2$ . Another issue is whether we should make use of equation of state models and corresponding fugacity models that have been developed specifically for  $D_2$ . And if we do make use of a model that is specific to  $D_2$ , would we expect the difference between a  $D_2$  model and an  $H_2$  model to be reliable in capturing the difference between the two gasses?

#### 4.1. Data of Michels et al. [8]

One place to begin the discussion is with the measurements at “low” pressure reported by Michels et al. [8] which are shown in terms of the compression ratio in Fig. 6. At low pressure there does not appear to be a discernible difference in the compression ratio, as would probably be expected since the deviation from the ideal gas compressibility is small, and the difference between deuterium and hydrogen volumes are minimal. At higher pressure, in the vicinity of 0.3 GPa one could argue for a per cent level difference, favoring a larger volume for  $H_2$  as expected due to zero-point nuclear motion contributions.

#### 4.2. Fits of Mills et al. [9,10]

Next we consider the fit for  $H_2$  given in Mills et al. [9], and an equivalent one for  $D_2$  given in Mills et al. [10]. The two fits are

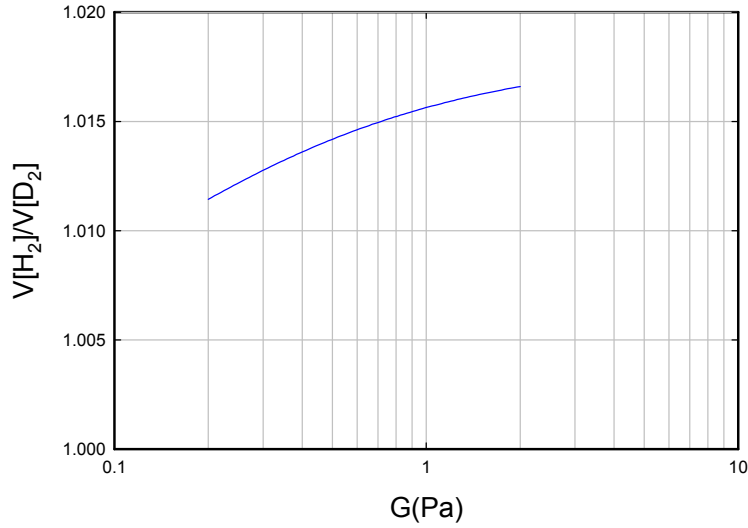
$$V[\text{H}_2] = \left( 36.716 + 0.0033003T - \frac{22.479}{\sqrt{T}} \right) P^{-1/3} + \left( -17.174 - 0.021393T \right) P^{-2/3} + \left( -8.9886 + 0.11001T + \frac{69.233}{\sqrt{T}} - \frac{31.395}{T} \right) P^{-1}, \quad (21)$$

$$V[\text{D}_2] = \left( 35.283 + 0.00094704T + \frac{3.2843}{\sqrt{T}} \right) P^{-1/3} + \left( -25.090 + 0.0063917T \right) P^{-2/3} + \left( 13.650 + 0.069563T - \frac{158.29}{\sqrt{T}} + \frac{720.00}{T} \right) P^{-1} \quad (22)$$

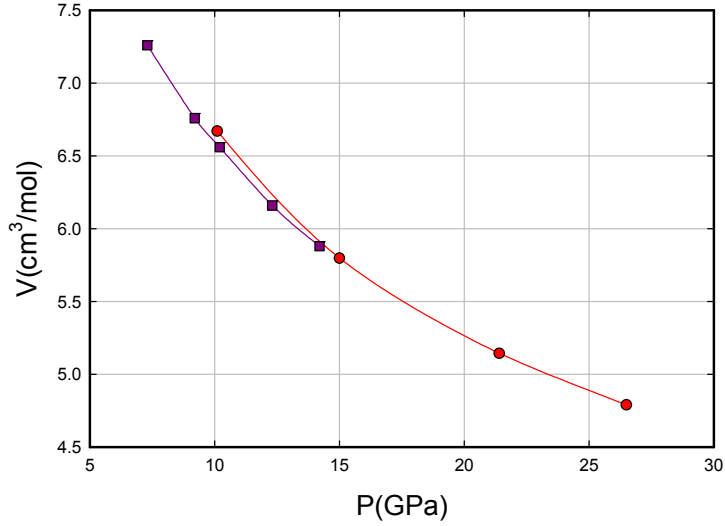
with  $P$  in kbar and  $V$  in  $\text{cm}^3/\text{mol}$ . The ratio  $V[\text{H}_2]/V[\text{D}_2]$  is shown as a function of pressure at 300 K between 2 and 20 kbar in Fig. 7. One observes that there is a volume increase for  $\text{H}_2$  over  $\text{D}_2$  on the order of 1.5%.

#### 4.3. Data of Hemley et al. [15]

Also relevant to the discussion appears to be the  $PVT$  measurements of Hemley et al. [15] done for  $\text{H}_2$  and for  $\text{D}_2$ , taken above the liquid/solid phase boundary. One can see from the data points plotted in Fig. 8 that the  $\text{H}_2$  volume is larger than the  $\text{D}_2$  volume, by a bit more than 1% near 10 GPa. This seems to be generally consistent with the ratio obtained from Mills [9,10].



**Figure 7.** Plot of the ratio  $V[\text{H}_2]/V[\text{D}_2]$  as a function of pressure at 300 K based on the fits of Mills [9,10].



**Figure 8.** Data points for  $V$  as a function of  $P$  at 300 K of Hemley et al. [15]. The upper curve with right circles is for  $H_2$ , and the lower curve with dark pink squares is for  $D_2$ .

#### 4.4. Model of Tkacz and Litwiniuk [27]

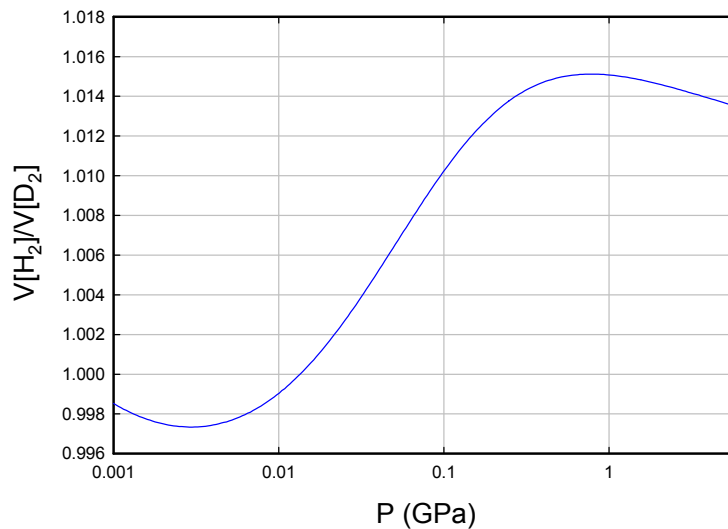
Tkacz and Litwiniuk fitted data separately for both  $H_2$  and for  $D_2$ . The equation of state model is based on Eq. (4), with the fitting parameters of Table 5. We note the issue that the form of the fit used does not go to the ideal gas law for  $P \rightarrow 0$ , and that this introduces issues in both the equation of state and the fugacity. Results for the ratio of the volumes as a function of pressure are shown in Fig. 9. One observes that the ratio is generally consistent with experiment at high pressure, but is unreliable at low pressure.

#### 4.5. Model of Joubert and Thiebaut [32]

In the discussion above we found that the empirical model of Joubert [31] seemed to be the best of the lot. A similar equation of state model for  $D_2$  was developed subsequently [32]. This equation of state model is given by Eq. (5) with fitting parameters given in Table 6.

**Table 5.** Fitting parameters for the equation of state of  $D_2$  based on the Tkacz and Litwiniuk model [27]; the pressure is in MPa, and the volume is in  $cm^3/mol$ .

Parameter	Value
$A$	174.725
$B$	-643.463
$C$	-334.258
$D$	763.862
$E$	8.63927

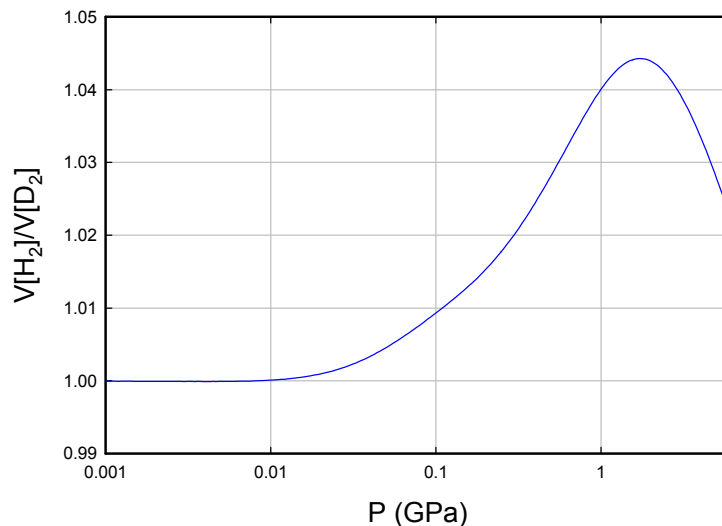


**Figure 9.** Plot of the ratio  $V[\text{H}_2]/V[\text{D}_2]$  as a function of pressure at 300 K based on the fits of the fits of Tkacz and Litwiniuk [27].

Results are shown in Fig. 10. The ratio in this case looks good at low pressure, and increases in a plausible way at somewhat higher pressures. However, the peak ratio goes up over 1.04, which seems too high relative to the experimental data discussed above. Our conclusion in this case is that these most recent models probably overestimate the difference between  $\text{H}_2$  and  $\text{D}_2$  at room temperature.

**Table 6.** Fitting parameters for the equation of state of  $\text{D}_2$  based on the model of Joubert and Thiebaut [32]; the pressure is in Pa, and the volume is in  $\text{m}^3/\text{mol}$ .

Parameter	Value
$a_1$	$4.86 \times 10^{-6}$
$a_2$	$5.46 \times 10^{-6}$
$a_3$	$4.342 \times 10^{-6}$
$a_4$	$-0.94 \times 10^{-6}$
$a_5$	$-1.79 \times 10^{-6}$
$b_1$	$5.35 \times 10^8$
$b_2$	$4.21 \times 10^9$
$b_3$	$3.99 \times 10^{10}$
$b_4$	$2.90 \times 10^7$
$b_5$	$8.02 \times 10^7$
$c$	$2.434 \times 10^{-6}$
$R$	8.31451



**Figure 10.** Plot of the ratio  $V[\text{H}_2]/V[\text{D}_2]$  as a function of pressure at 300 K based on the fits of the fits of Joubert [31] and Joubert and Thiebaut [32].

#### 4.6. Discussion

From the experimental data sets discussed above we would expect the  $\text{H}_2$  volume to be larger than the  $\text{D}_2$  volume by up to about 1.5% near 1 GPa. The empirical models of Tkacs and Litwiniuk [27] are consistent with this around 1 GPa, but have issues at lower pressure. The recent models of Joubert [31] and Joubert and Thiebaut [32] are good at low pressure, but overestimate the difference at higher pressure.

Suppose we wished to study the difference between  $\text{H}_2$  and  $\text{D}_2$  in connection with PdH and PdD near room temperature, and we wanted to understand what difference came about due to differences in the fugacity, then how might we proceed? Based on the discussion above, one way might be to make use the difference in volume at high pressure based on the Tkacs and Litwiniuk [27] equation of state models (use a cut-off factor to suppress the errant low-pressure anomaly), and then use this to modify the Joubert [31]  $\text{H}_2$  equation of state to  $\text{D}_2$ .

### 5. Theoretical Issues

One could imagine starting with the equation of state model for  $\text{H}_2$  of Joubert [31], and then estimating the difference between  $\text{H}_2$  and  $\text{D}_2$  based on a theoretical model. For example, if one believed that the nuclear zero-point contribution to the equation of state was dominant, it would be possible to develop and estimate of the difference, and then use this estimate to correct the  $\text{H}_2$  equation of state to make it applicable for  $\text{D}_2$ .

Unfortunately, the situation is more complicated than this, as we will see in this section. Moreover, this problem in general has been of interest to researchers in the literature, and it seems worthwhile to think some about the issues involved.

### 5.1. Absence of a mass difference in a simple classical model

It is possible to make some progress by considering first a classical version of the model in which the interaction potential between two H<sub>2</sub> molecules is the same as the interaction potential between two D<sub>2</sub> molecules. In this case we can compute the pressure from the classical partition function according to

$$P = k_{\text{B}}T \left[ \frac{\partial}{\partial v} \ln Z_{\text{C}} \right]_T. \quad (23)$$

The classical partition function in this case is given by

$$Z_{\text{C}} = \frac{1}{(\prod_k N_k!)} \frac{1}{h^{3n}} \int \dots \int e^{-H(\mathbf{r}_1 \dots \mathbf{r}_n, \mathbf{p}_1 \dots \mathbf{p}_n)/k_{\text{B}}T} d^3\mathbf{r}_1 \dots d^3\mathbf{r}_n d^3\mathbf{p}_1 \dots d^3\mathbf{p}_n, \quad (24)$$

which is a generalization of the identical molecule formula in Mayer [41]. The momentum integrations can be done analytically for the nonrelativistic version of the problem

$$\int \dots \int e^{-\sum_j |\mathbf{p}_j|^2/2m_j k_{\text{B}}T} d^3\mathbf{p}_1 \dots d^3\mathbf{p}_n = \prod_j \left( 2\pi m_j k_{\text{B}}T \right)^{3/2}. \quad (25)$$

The resulting contribution is independent of the volume  $V$ , and so does not contribute to the pressure. In this case, the classical pressure in a simple binary interaction model is given by

$$P = k_{\text{B}}T \left[ \frac{\partial}{\partial V} \ln \int \dots \int e^{-\sum_{j < k} U(\mathbf{r}_j - \mathbf{r}_k)/k_{\text{B}}T} d^3\mathbf{r}_1 \dots d^3\mathbf{r}_n \right]_T. \quad (26)$$

The pressure then in this kind of simple classical model is independent of the mass. This is the reason that we see such similar equation of state curves in the previous section.

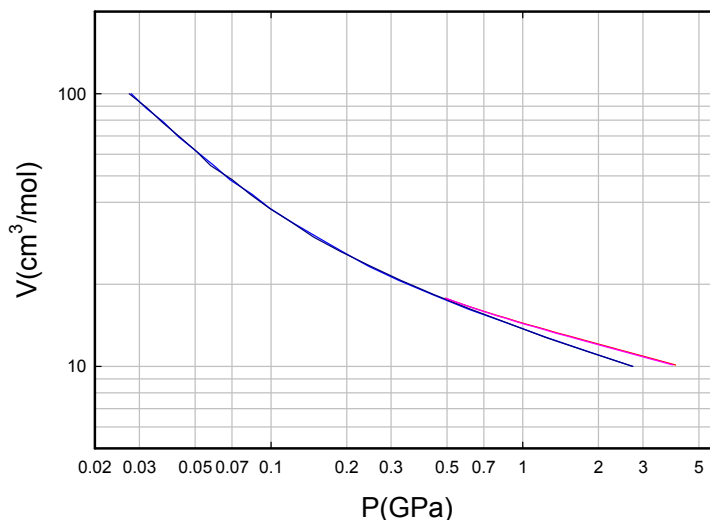
### 5.2. Pressure in a quantum mechanical model

In a quantum mechanical version of the problem the partition function can be defined according to

$$Z_{\text{Q}} = \sum_j g_j e^{-E_j/k_{\text{B}}T}, \quad (27)$$

where the summation is over the states of the (many-particle) quantum system. From this quantum mechanical partition function, we can determine the pressure as before

$$P = k_{\text{B}}T \left[ \frac{\partial}{\partial v} \ln Z_{\text{Q}} \right]_T. \quad (28)$$



**Figure 11.** Volume as a function of pressure for the Slater–Kirkwood exp-6 potential model of Ross et al. [43]; molecular dynamics for H (blue) and D (dark blue); quantum FCC cell model for H (red) and D (pink).

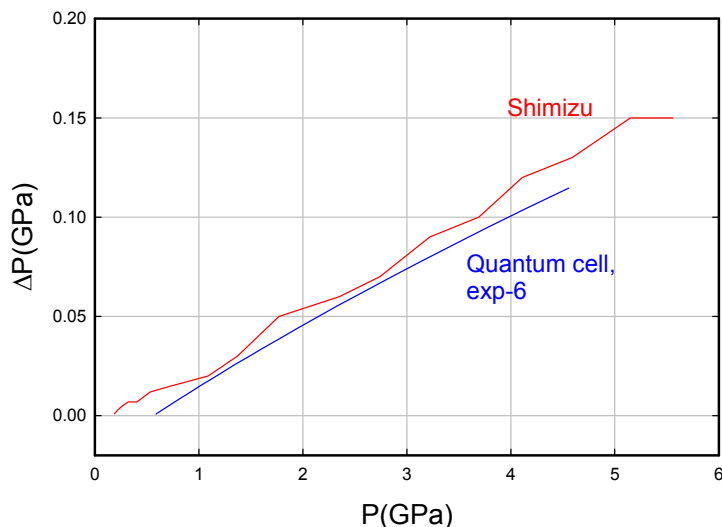
### 5.3. Computational results

We examined a specific model for the equation of state based on some classical and quantum mechanical models, in order to try to understand the theoretical problem better. For these calculations we used the Slater–Kirkwood [42] exp-6 model of Ross et al. [43]. For the classical equation of state we computed the pressure at a fixed volume for 200 molecules at room temperature based on a molecular dynamics calculation. As expected we obtained the same pressure for  $H_2$  and  $D_2$  to within the precision of the calculation (see Fig. 11). We worked with a number of different molecular potential models, and found that the Slater–Kirkwood exp-6 model of Ross et al. [43] gave the best agreement with the experimental equation of state at room temperature.

For the quantum mechanical equation of state, we modeled a single molecule as a quantum particle in a fixed FCC lattice with the same exp-6 potential model. The quantum calculation might be considered to be a numerical 3D quantum cell calculation with a realistic potential, as a generalization of the simpler quantum cell calculation used in years past from the literature [44–50]. For these calculations we solve the (discretized) Schrödinger equation directly for up to about 30,000 states, we construct the quantum mechanical partition function, and repeat for different volumes to allow a pressure calculation. The results are shown in Fig. 11.

For the quantum mechanical calculation, we found good agreement with the classical calculation at low pressure, and a systematic deviation from the classical model at higher pressures. This can be attributed to the use of a quantum cell model, in which the collisions between the test molecule and neighboring molecules at fixed locations are harder on average than had we allowed all of the molecules to move. We also found a higher pressure for  $H_2$  than  $D_2$  as a result of the difference in the nuclear zero-point motion at all but the largest volume used (where the computation is most demanding due to many excited state contributions which become difficult to compute accurately in a single calculation as we carried out).





**Figure 12.** Differential pressure for H<sub>2</sub> and D<sub>2</sub> as a function of H<sub>2</sub> pressure for the quantum cell calculation with the Slater–Kirkwood exp-6 potential model (blue); and from the calculations of Shimizu and Kumazawa [51].

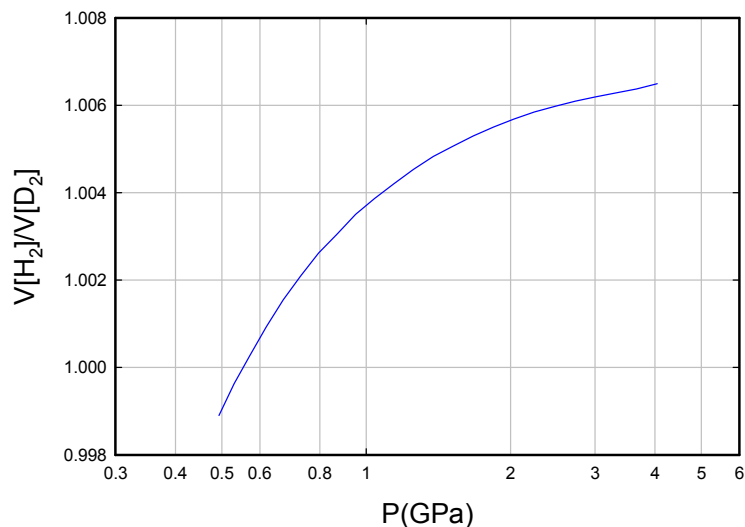
The difference in pressure between H<sub>2</sub> and D<sub>2</sub> was determined at different volumes from the quantum cell model (Fig. 12), with the results in reasonable agreement with the perturbation theory calculation of Shimizu and Kumazawa [51]. The ratio of the volumes from the cell model calculation is shown in Fig. 13. We see that the contribution of the zero-point nuclear motion yields a volume ratio that is less than what is observed in experiment.

#### 5.4. Difference in the binary potentials

We have argued that the zero-point contribution cannot account for the difference between the H<sub>2</sub> and D<sub>2</sub> equation of state, we must turn to other explanations. In this case there is another source of difference between the two problems which is perhaps more subtle, but which should be expected. At room temperature we would expect some degree of excitation of the rotational states. For example, keeping in mind that some of the rotational states are excluded because the overall wavefunction must be anti-symmetric, we can compute the average rotational excitation to be

$$\langle l \rangle = 1.213 \quad \text{H}_2, \quad \langle l \rangle = 1.856 \quad \text{D}_2. \quad (29)$$

In the case of the molecular hydrogen at near 0 K, the equation of state is different for *ortho*-H<sub>2</sub> and *para*-H<sub>2</sub> [52–54]. Since the masses are the same in this case, the differences can only be attributed to the differences in the inter-molecular potential which is known to differ for the different rotational states. Models for the inter-molecular potential have been developed for some of the low-lying rotational states [55–58]. However, what would be helpful would be an inter-molecular potential model averaged appropriately over the degree of rotational excitation. Such a model would be very useful for the computation of differences between H<sub>2</sub> and D<sub>2</sub>.



**Figure 13.** Ratio of  $V[\text{H}_2]/V[\text{D}_2]$  as a function of  $\text{H}_2$  pressure from the quantum cell model.

## 6. Discussion and Conclusions

To interpret experimental results for the loading as a function of pressure, and to understand the chemical potential of hydrogen or deuterium in metals, reliable models for the fugacity are needed. This problem has been of interest now for almost 80 years, so much work has been focused on the problem generally. In the earliest modeling efforts, it was sufficient to make use of an ideal gas model for hydrogen gas and deuterium gas. However, to model the Fleischmann–Pons experiment we are interested in understanding the chemical potential at a loading near unity, which means that we need to understand the equation of state and the fugacity at pressures up to and beyond 1 GPa.

Fortunately, there are available many experimental studies of the  $\text{H}_2$  equation of state in the regime of interest, and fewer studies of the  $\text{D}_2$  equation of state. The model of Tkacz and Litwiniuk [27] has been important in recent years; however, it is not widely appreciated that the fit employed leads to a divergence from ideal gas relations at low pressure. We noticed differences in the fugacity larger than expected a few years ago [59] when we compared it with results published by Bockris et al. [7] based on the model of Holley et al. [19]. The more recent model of Joubert [31] represents a significant improvement.

In times past people would use the  $\text{H}_2$  fugacity freely for  $\text{D}_2$ , since one would expect the differences to be small. However, in recent years there have become available equation of state and fugacity models that are specific to  $\text{D}_2$ , which is of great interest for precision thermodynamic modeling. We were interested in whether the differences in the  $\text{H}_2$  and  $\text{D}_2$  models is reliable, in the sense of being reflected in the equation of state data. In the models of Tkacz and Litwiniuk [27], the difference at room temperature near 1 GPa seems close to the difference seen in experiment. However, the same does not seem to be true for the more recent models of Joubert [31] and Joubert and Thiebaut [32].

Since the differences are small, we thought that it might be possible to arrange for an estimate of the difference based on theory. For example, one can contemplate developing a reliable estimate for the zero-point contribution to the equation of state. As we have seen, this contribution is only part of the difference. The remainder is due to differences

in the inter-molecular potential. In principle this could be calculated, if a suitable rotationally averaged inter-molecular potential were available. At present such a model does exist. In the future we would expect such models to be of interest, and once available one might return to the problem of developing a theoretical estimate for the difference in equation of state models.

Given the present situation, probably the most reliable approach to fugacity models that can address differences between the H<sub>2</sub> and D<sub>2</sub> fugacity would be to work with the difference between the two equation of state models of Tkacz and Litwiniuk [27], use a cut-off at low pressure, and then use this difference with the model of Joubert [31] to obtain equation of state and fugacity values for D<sub>2</sub>.

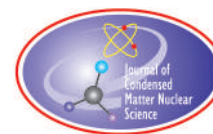
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Research Article

# Deuterium Evolution Reaction Model and the Fleischmann–Pons Experiment

Peter L. Hagelstein\*

*Massachusetts Institute of Technology, Cambridge, MA 02139, USA*

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## Abstract

The hydrogen evolution reaction model was proposed many years ago by the founders of modern electrochemistry. The closely related deuterium evolution reaction model describes deuterium loading in Pd cathodes in the Fleischmann–Pons experiment. We were interested in what issues were involved in the development of a high D/Pd loading, since over the years the importance of obtaining a high D/Pd ratio to obtain excess heat has been emphasized. In order to simplify things, we focus on the Volmer and Tafel reactions, and develop a steady state adsorption isotherm for the Vomer-Tafel regime. The adsorption isotherm is extended to become an absorption isotherm within a simplified picture that takes the surface sites to be equivalent to the bulk sites. While not a particularly good approximation, this allows us to model the D/Pd loading simply as a function of the overpotential, and hence the electrochemical current density. From a Tafel curve we can get some of the parameters for the Volmer current model, and from other electrochemical data we can estimate the remaining Volmer and Tafel parameters. The resulting model fits the experimental data used well at low current density. Cathodes that load more highly with this approach require new models, potentially one for each cathode. We examine our earlier proposal that the differences in loading seen in experiment is due in part to large variations in the rate for internal D<sub>2</sub> leaks. Consequently, we modify the Tafel reaction current model to account for internal leaks separately from the surface gas loss, and take advantage of data from the most highly loaded cathodes to estimate the surface Tafel reaction rate. Using this approach, the reference cathode that we used for our fits initially must have an internal leak rate more than two orders of magnitude higher than the rate of surface D<sub>2</sub> loss. We conclude that minimizing the internal leaks is important in achieving high loading. Probably a key reason that there were so many negative results early in the field was because the cathode internal leak rate was very high in the cathodes used.

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*Keywords:* Deuterium evolution reaction, D/Pd loading, Overpotential, Tafel reaction, Volmer reaction

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## 1. Introduction

Excess heat in the Fleischmann–Pons experiment [1,2] is an effect which should not exist according to what is currently accepted in mainstream nuclear physics and condensed matter physics. We have been interested in developing a basic understanding of the experiment for many years [3]. From our perspective, part of the problem has to do with what

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\*E-mail: plh@mit.edu

kind of new physical process is involved that allows the conversion of nuclear energy to excitation in non-nuclear degrees of freedom which subsequently thermalizes; and part of the problem has to do with more conventional aspects of the problem which are amenable to analysis based on established science. In this paper our focus is on a more conventional part of the problem; in particular we are concerned with some of the the basic electrochemical issues associated with the development of high deuterium loading.

The need for high deuterium loading in Pd in the Fleischmann–Pons experiment as a prerequisite for the development of excess heat was recognized by Fleischmann and Pons (although one might take exception to the discussion of a chemical potential as high as 0.8 eV, as mentioned in the opening paragraphs of [1]). This requirement has been emphasized by McKubre and coworkers repeatedly over the years [4–7]. At issue then is the basic question of what is needed to obtain a high D/Pd loading ratio. A more general issue concerns how to model the deuterium loading in the Fleischmann–Pons experiment, perhaps as part of a more complete simulation of the excess heat effect model in which we are interested.

Of course, the electrochemistry associated with loading hydrogen or deuterium into Pd or other cathode metals has been of interest for decades. Early contributions to the theory and mechanisms are found in the early papers by Eyring and coworkers [8–10], and Frumkin and coworkers [11,12], and Bockris and coworkers [13–16]. Out of this early work developed models in use today, which goes by the name “hydrogen evolution reaction.” It appears to have been Bockris that first used this phrase in the literature [16,17].

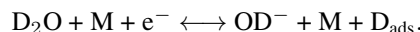
There have been a number of papers published on modeling relevant to the loading of deuterium in connection with the Fleischmann–Pons experiment [18–30]. In principle one would expect that by using the hydrogen evolution reaction model, and perhaps some account of diffusion, that all of the major issues associated with obtaining high loading in the Fleischmann–Pons experiment could be clarified. One of our goals in this discussion is to understand the relevant issues better.

## 2. Volmer–Tafel Regime Mechanisms

It would be possible to begin by simply implementing the hydrogen evolution equations for deuterium (in which case we would speak of the deuterium evolution equations), modeling deuterium diffusion in the cathode, and then comparing the results to experiment. We have carried out such an effort, and in the process we have understood that there are various issues that need to be addressed before such modeling is likely to be helpful and illuminating. Consequently, it will be useful to first simplify the problem, and focus on the low (cathodic) current density regime in which only the Volmer and Tafel reactions are needed (the Volmer–Tafel regime).

### 2.1. Basic reaction mechanisms in the Volmer–Tafel regime

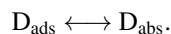
The loading of deuterium in palladium can be understood simply enough in a broad sense in terms of individual reactions that constitute the hydrogen/deuterium evolution reaction model. Deuterium is brought to the surface through the alkaline version of the Volmer reaction



Deuterium on the surface can recombine through the Tafel reaction to make  $\text{D}_2$  gas



Adsorbed deuterium can move into the cathode to occupy more tightly bound sites associated with absorbed deuterium



Other things can happen as well (such as the Heyrovsky reaction and surface coverage by impurities). However, these basic reactions provide a simple picture which allows for a quantitative description of the cathode loading at low current density.

## 2.2. Loading in the Volmer–Tafel regime

In this reduced picture, the electrochemical current is dominated at the Pd surface by the Volmer reaction. When this occurs, one deuterium atom is deposited on the cathode surface as an adsorbed atom per charge transferred. In this regime, we can load the cathode simply by applying a current. As deuterium accumulates on the surface (and hence in the bulk), the deuterium chemical potential increases, making  $D_2$  gas formation more likely. The loading is determined in the Volmer–Tafel regime by matching the incoming deuterium from the Volmer reaction to the outgoing deuterium gas associated with the Tafel reaction.

## 2.3. Volmer reaction kinetics model

We start with a model for the Volmer current density  $j_V$  given by [24]

$$j_V = rj_{V0} \frac{1-\theta}{1-\theta_0} e^{-(1-\beta_V)f\eta} e^{-\delta_V u(\theta-\theta_0)} + db, \quad (1)$$

where we follow Ref. [24] most closely. Here  $r$  is a roughness factor,  $\theta$  is the fraction of available surface sites with adsorbed deuterium,  $\beta_V$  is an asymmetry factor,  $f$  is defined by

$$f = \frac{|e|}{k_B T} = \frac{F}{RT} \quad (2)$$

and  $\eta$  is the overpotential. The  $u$  parameter is a heterogeneity factor of Frumkin adsorption, and  $\delta_V$  is a symmetry factor. We have included the forward (loading term) explicitly; the notation  $db$  denotes the (de)loading counter term required for detailed balance. The magnitude of the current density is determined by the parameter  $j_{V0}$  which is to be determined from experimental data taken at a loading of  $\theta_0$ .

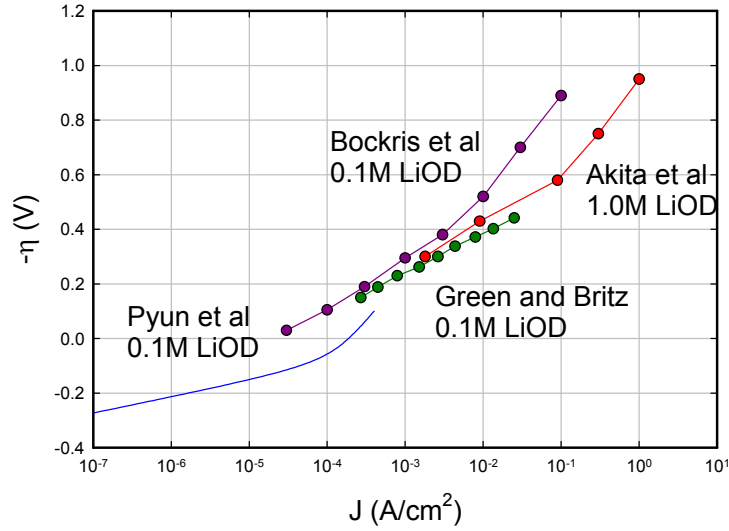
It is worthwhile to think about this model before proceeding. We have exhibited the contribution to the Volmer current density due to the forward pathway, in which deuterium atoms are left adsorbed on the surface, which contributes to loading (and dominates over the inverse reaction under conditions of interest to us). Consequently, we expect to see a proportionality to  $(1-\theta)$ , which accounts for an inability for the reaction to proceed if all the surface sites are occupied, and a reduction in the loading rate when the surface loading is already high. We recognize the exponential factors associated with statistical mechanics  $\exp(\Delta G/k_B T)$  terms, one for the electron exchange ( $e^{-(1-\beta_V)f\eta}$ ), and one for deuterium atom exchange ( $e^{-\delta_V u(\theta-\theta_0)}$ ).

## 2.4. Tafel plot

We are interested in obtaining values for the fitting parameters associated with the Volmer current density. It is possible to develop an estimate for the asymmetry factor  $\beta_V$  from a Tafel plot. To proceed, we note that under cathodic conditions the Volmer current density is dominated by the first term so that

$$j_V \rightarrow rj_{V0} \frac{1-\theta}{1-\theta_0} e^{-(1-\beta_V)f\eta} e^{-\delta_V u(\theta-\theta_0)}. \quad (3)$$





**Figure 1.** Tafel plots from Pyun et al. [37] (blue line); from Bockris et al. [35]; from Akita et al. [38]; and from Green and Britz [39].

This expression simplifies when we consider the special case where  $\theta = \theta_0$ ; in this case we may write

$$j_V \rightarrow r j_{V0} e^{-(1-\beta_V)f\eta}. \quad (4)$$

At this preferred constant loading, the  $\ln$  of the Volmer current density is linear in the overpotential. From experiments it is possible to construct such a curve from measurements (a Tafel plot) and from this determine  $\beta_V$  and  $j_{V0}$  if  $r$  has been fixed.

In looking over the literature on Tafel plots for Pd, one finds the early papers mostly focused on Tafel plots for Pd in acid [31–33], for which the Volmer mechanism is different that discussed above. There appears to be one early paper that talks about an alkaline electrolyte [34], but the most interesting studies with alkaline electrolytes for us are much more recent [45–41]. Tafel plots from some of the experiments done in LiOD are shown in Fig. 1.

The asymmetry factor  $\beta_V$  can be obtained from the slope of the Tafel plot at low current density, and Green and Britz [39] give a value of 0.49 for 0.1 M LiOD; however, we will end up with better self-consistency with the simple model of the next section with a value of  $\beta_V = 0.48$ . For simplicity, we have adopted  $r = 2$  obtained from capacitance measurements as described in this work. We are able to approximately match the data given in this paper with

$$j_{V0} = 1.70 \times 10^{-5} \text{ A/cm}^2 \quad (5)$$

and

$$\theta_0 = 0.70. \quad (6)$$

This choice in our models approximately reproduces the overpotentials that are reported in [39]. At high current density in some of the curves of Figure 1 there is a change in slope where the Volmer contribution to the electrochemical current density is no longer dominant.

## 2.5. Surface Tafel reaction model

In the case of the Tafel reaction, we can begin with a model for the equivalent Tafel current density  $j_T$  given by

$$j_T = r^2 j_{T0} \left( \frac{\theta}{\theta_0} \right)^2 e^{2(1-\delta_T)u(\theta-\theta_0)} + \text{db.} \quad (7)$$

Here  $u$  is a Frumkin adsorption isotherm parameter [24], which takes into account the change in the chemical potential of the deuterium with loading, under conditions where the deuterium chemical potential is linear in  $\theta$ . The parameter  $\delta_T$  is a symmetry parameter associated with the Tafel reaction.

It is useful here to consider this parameter a bit further. For example, we might parameterize the change in Gibbs free energy associated with the transfer of a single deuterium atom in the vicinity of a reference loading ( $\theta_0 = 0.70$  in this case) according to

$$\Delta G = \Delta G_0 + (\theta - \theta_0) \frac{\partial \Delta G}{\partial \theta} + \dots \quad (8)$$

If so, the associated statistical exponential factor is

$$\exp \left\{ \frac{\Delta G}{RT} \right\} \approx \exp \left\{ \frac{\Delta G_0}{RT} \right\} \exp \left\{ \frac{1}{RT} (\theta - \theta_0) \frac{\partial \Delta G}{\partial \theta} \right\}. \quad (9)$$

The zero-order term is captured within the prefactors of the model; the first order term remains explicitly, and we can identify  $u$  with

$$u = \frac{1}{RT} \frac{\partial \Delta G}{\partial \theta}. \quad (10)$$

In the beta phase, we can make use of the room temperature measurements of Chun and Ra [42], which leads to

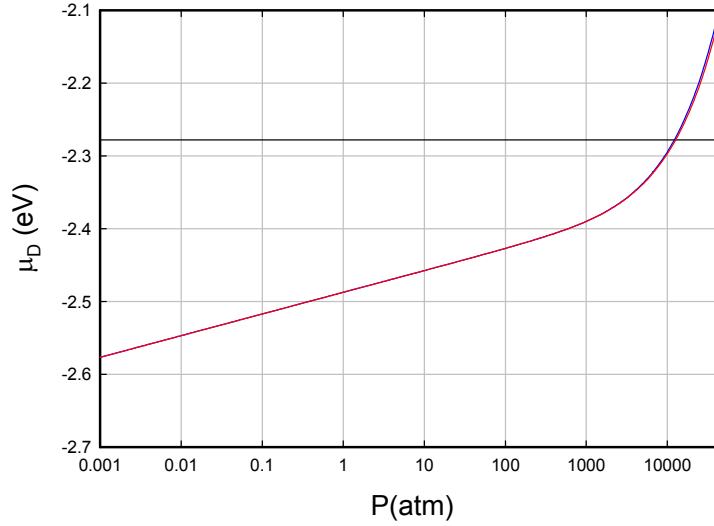
$$u = 20.0. \quad (11)$$

## 2.6. Deuterium chemical potential

In connection with the estimate for the Frumkin adsorption isotherm parameter from above, it seems useful to consider the chemical potential for deuterium in Pd. The argument rests on experiments in which palladium comes into equilibrium with deuterium gas at a given temperature and pressure, and the loading is determined. In equilibrium the chemical potentials are equalized. Since the chemical potential of gas phase deuterium is known accurately, it is possible to determine the chemical potential of deuterium in PdD from such measurements.

The chemical potential of molecular  $D_2$  satisfies

$$\frac{\mu_{D_2} + E_d}{k_B T} = -\ln z_{\text{nonideal}} - \ln z_{\text{rotvib}}, \quad (12)$$



**Figure 2.** Deuterium chemical potential at 300 K as a function of pressure; with the  $D_2$  fugacity from Joubert and Thiebaut [44] (red line); with the  $H_2$  fugacity from Joubert [43] (blue line); and half the dissociation energy  $-E_d/2$  (black line).

where  $\mu_{D_2}$  is the chemical potential, where  $E_d$  is the dissociation energy, where  $z_{\text{nonideal}}$  is the nonideal gas partition function, and where  $z_{\text{rotvib}}$  is the rotational and vibrational partition function. For the nonideal gas partition function we may write

$$\frac{1}{z_{\text{nonideal}}} = \frac{f_{D_2}}{k_B T} \left( \frac{2\pi\hbar^2}{Mk_B T} \right)^{3/2}. \quad (13)$$

where  $f_{D_2}$  is the fugacity of  $D_2$  gas. For the rotational and vibrational partition function we have

$$z_{\text{rot}} = 6 \sum_{\text{even } l} \sum_n (2l+1) e^{-E_{nl}/k_B T} + 3 \sum_{\text{odd } l} \sum_n (2l+1) e^{-E_{nl}/k_B T}, \quad (14)$$

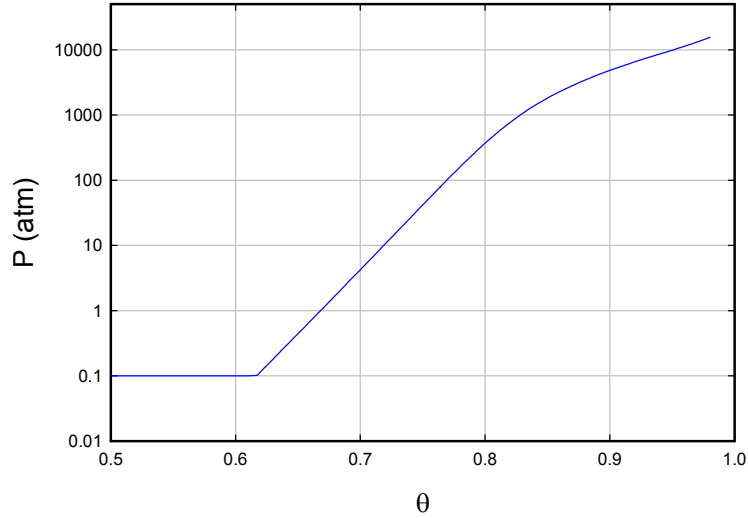
where in writing this we have included the nuclear spin degeneracies explicitly.

The chemical potential for atomic deuterium in  $D_2$  can be related to the  $D_2$  chemical potential through

$$\mu_D = \frac{1}{2}\mu_{D_2} = -\frac{1}{2}k_B T \left( \ln z_{\text{nonideal}} + \ln z_{\text{rotvib}} \right) - \frac{E_d}{2}. \quad (15)$$

The deuterium chemical potential at 300 K is shown in Fig. 2 as a function of pressure.

We can use this to determine the chemical potential of D in PdD, by starting with the absorption isotherm for PdD. An absorption isotherm for 30°C has been constructed from data available in the literature [43–46], which is shown in Fig. 3. We can convert this isotherm from pressure to chemical potential following the discussion above to obtain an estimate for the chemical potential as a function of loading in Fig. 4. There is little difference in the chemical potential



**Figure 3.** Absorption isotherm for deuterium in Pd at 30°C.

based on fugacity models for H<sub>2</sub> [43] and D<sub>2</sub> [44]. From this we can estimate the change in deuterium chemical potential with  $\theta$  to obtain

$$\left(\frac{\partial\mu_{\text{D}}}{\partial\theta}\right)_T = 0.573 \text{ eV} \quad (16)$$

from a least squares fit to the data above the miscibility gap. From this we would estimate a Frumkin adsorption isotherm parameter

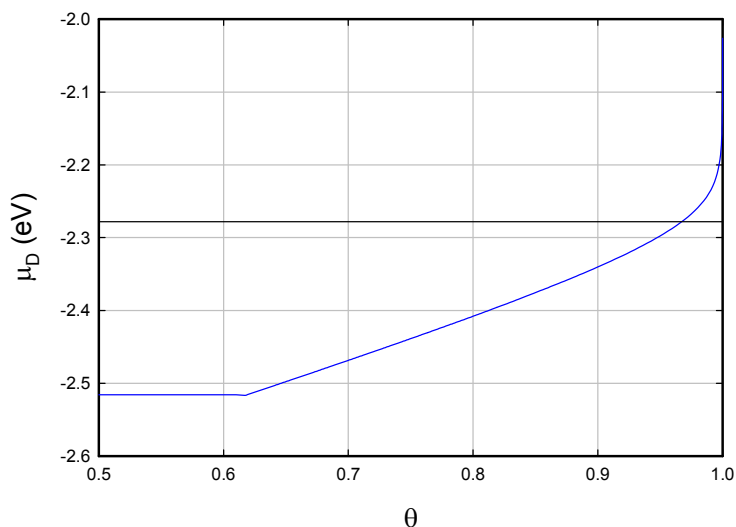
$$u = \frac{1}{k_{\text{B}}T} \left(\frac{\partial\mu_{\text{D}}}{\partial\theta}\right)_T = 22.2, \quad (17)$$

which is in reasonable agreement with the value  $u = 20$  found from the measurements of Chun and Ra [42].

## 2.7. Discussion

In this section we have outlined the Volmer model for the current density associated with deuterium adsorption under cathodic conditions in an alkaline electrolyte, and the Tafel model which describes molecular D<sub>2</sub> formation from adsorbed deuterium atoms on the surface. From the simplest point of view, cathode loading occurs through the Volmer reaction, and de-loading occurs through the Tafel reaction, all in the Volmer–Tafel regime.

The form of the models is dictated by a combination of statistical mechanics and quantum mechanics, with empirical parameters which can be fit to model one or more cathodes. Data from a Tafel plot allows us to specify  $j_{V0}$  and  $\beta_V$  at a given loading  $\theta_0$ , once an estimate for the surface roughness factor is available from other measurements. The



**Figure 4.** Deuterium chemical potential as a function of D/Pd at 30°C (blue);  $-E_d/2$  (black).

model as written presumes a linear dependence of the chemical potential on the loading, which we see is approximately the case above the miscibility gap. We have an estimate for the slope from electrochemical experiments [42], and also from loading measurements of Pd in  $D_2$  gas. We could upgrade these models by making use of the chemical potential as a function of loading with little difficulty.

It remains to determine the prefactor for the Tafel current density, and also to determine the symmetry factor associated with the chemical potential. This will require fitting to experimental loading data in the Volmer–Tafel regime.

### 3. Steady State Conditions and Isotherm

The models discussed above are known to be sufficient to provide a reasonable description of steady state loading at low current density. We presume in connection with this discussion that the chemical potential of the surface matches the chemical potential of the bulk in steady state, so that the surface coverage in this idealized model matches the bulk loading. We can obtain an explicit expression for the adsorption isotherm in this case, which in this simple picture gives the bulk loading as a function of the overpotential.

#### 3.1. The Volmer–Tafel isotherm

Under steady state conditions the incoming deuterium from the Volmer reaction must be balanced by the outgoing  $D_2$  gas from the Tafel reaction. This leads to the condition

$$j_V = j_T. \quad (18)$$

If we assume that the forward Volmer term associated with loading is dominant, and the forward Tafel term associated with deloading is dominant, then we can write

$$r j_{V0} \frac{1-\theta}{1-\theta_0} e^{-(1-\beta_V)f\eta} e^{-\delta_V u(\theta-\theta_0)} = r^2 j_{T0} \left(\frac{\theta}{\theta_0}\right)^2 e^{2(1-\delta_T)u(\theta-\theta_0)}. \quad (19)$$

It will be convenient to rewrite this isotherm as

$$\left(\frac{1-\theta}{1-\theta_0}\right) \left(\frac{\theta}{\theta_0}\right)^2 e^{-(2+\delta_V-2\delta_T)u(\theta-\theta_0)} = r \frac{j_{T0}}{j_{V0}} e^{(1-\beta_V)f\eta}. \quad (20)$$

### 3.2. Overpotential in steady state at $\theta = \theta_0$

At the reference loading  $\theta = \theta_0$  the adsorption isotherm reduces to

$$1 = r \frac{j_{T0}}{j_{V0}} e^{(1-\beta_V)f\eta_0}, \quad (21)$$

where  $\eta_0$  is defined to be the steady-state overpotential consistent with  $\theta_0$  according to Eq. (20). In the experiments described by Green and Britz [39] a loading of 0.70 for 0.1 M LiOD corresponds to about 0.6 mA/cm<sup>2</sup>, and  $\eta_0 = -0.15$  V at 303 K. Presumably for a different cathode in a different experiment one would obtain a different value for  $\eta_0$ . We can use the adsorption isotherm at this point to develop a relation for the Tafel current prefactor

$$j_{T0} = \frac{j_{V0}}{r} e^{-(1-\beta_V)f\eta_0}. \quad (22)$$

For the parameters assembled so far we estimate

$$j_{T0} = 1.69 \times 10^{-4} \text{ A/cm}^2. \quad (23)$$

### 3.3. Incremental loading and incremental overpotential

Consider now the incremental change in loading for an incremental change in the overpotential. We set

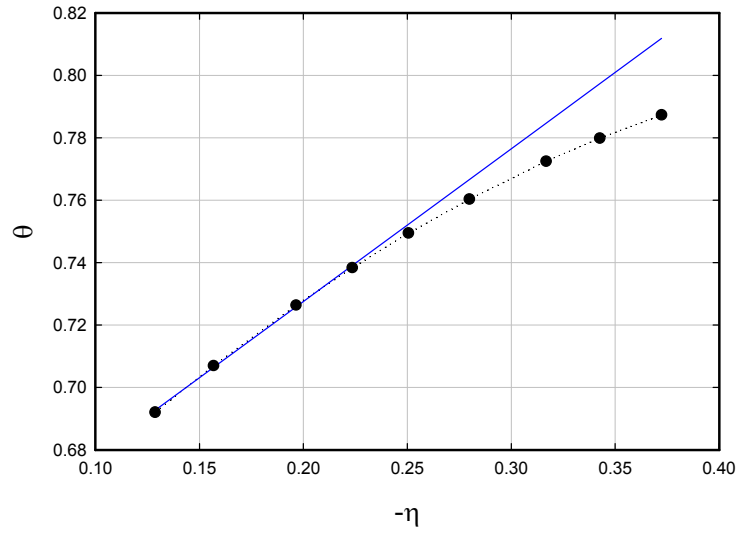
$$\theta = \theta_0 + d\theta, \quad (24)$$

$$\eta = \eta_0 + d\eta, \quad (25)$$

where  $d\theta$  is the incremental loading and  $d\eta$  is the incremental overpotential. Around equilibrium the adsorption isotherm satisfies

$$-\left[(2+\delta_V-2\delta_T)u + \frac{1}{1-\theta_0} + \frac{2}{\theta_0}\right]d\theta = (1-\beta_V)f d\eta. \quad (26)$$

From this we can write for the slope of the isotherm



**Figure 5.** Loading as a function of overpotential from the data of Green and Britz [39] for 0.1 M LiOD.

$$\frac{d\theta}{d\eta} = - \frac{(1 - \beta_V)f}{(2 + \delta_V - 2\delta_T)u + \frac{1}{1 - \theta_0} + \frac{2}{\theta_0}}. \quad (27)$$

### 3.4. Estimation of the symmetry parameters

For loading as a function of overpotential from Green and Britz [39] for PdD in 0.1 M LiOD shown in Fig. 5 we can develop a linear fit at low loading, and hence low current density Volmer–Tafel regime of the form

$$\theta(\eta) = 0.489422(-\eta + 1.28668). \quad (28)$$

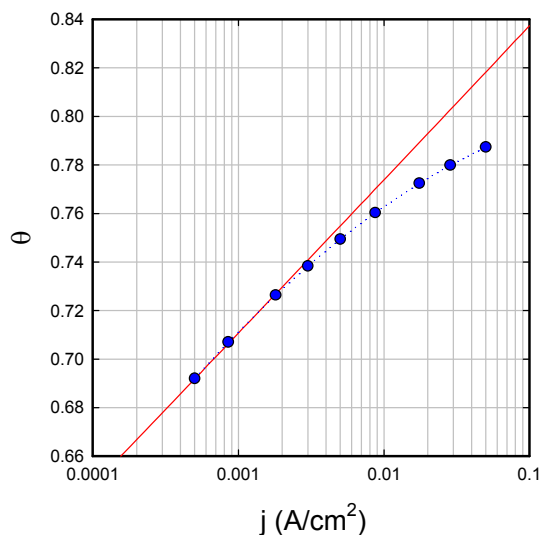
Consequently, we arrive at the constraint

$$\frac{(1 - \beta_V)f}{(2 + \delta_V - 2\delta_T)u + \frac{1}{1 - \theta_0} + \frac{2}{\theta_0}} = 0.489. \quad (29)$$

This leads to the constraint

$$\delta_V - 2\delta_T = -0.312. \quad (30)$$

Since we would like for  $\delta_V$  and  $\delta_T$  both to be positive, we choose



**Figure 6.** Loading as a function of electrochemical current density from the data of Green and Britz [39] for 0.1 M LiOD (blue circles); from the simple Volmer–Tafel isotherm of this section (red line).

$$\delta_V = 0, \quad (31)$$

$$\delta_T = 0.156. \quad (32)$$

### 3.5. Loading as a function of electrochemical current density

We can make use of the model parameters discussed in this section and the previous section to develop a model loading as a function of current density. The result is shown in Fig. 6 along with data points from Green and Britz [39]. One can see that the model matches experiment at low current density. At higher current density the loading is seen to be below the Volmer–Tafel regime model. This is indicative of additional processes beginning to become important at higher current density. For example, Zhang [24] discusses a model in which the Heyrovsky reaction pathway is proposed to account for the reduction of loading at higher current density. Also, Bockris proposes that the change in slope observed in the Tafel curve at high current density may be due to electrochemical desorption (Heyrovsky reaction) [40].

### 3.6. Discussion

We have considered perhaps the simplest possible model for the cathode loading under steady-state conditions by assuming essentially that the bulk sites are equivalent to the surface sites, and in steady state have equal occupation.



By including only the forward terms of the Volmer and Tafel current densities and setting them equal, we obtain an adsorption isotherm which is for us an absorption isotherm if bulk and surface sites are taken to be equivalent.

From matching the model to Tafel curve data, we are able to estimate  $\beta_V$  and  $j_{V0}$  as outlined in the previous section. From either the chemical potential as a function of loading, or from the voltametry studies of Chun and Ra [42] we have an estimate for  $u$ . From a comparison of the model with the electrochemical measurements of Green and Britz [39] we are able to develop estimates for the remaining model parameters  $j_{T0}$ ,  $\delta_V$  and  $\delta_T$  systematically.

The basic conclusion so far is that we are able to take advantage of a subset of the deuterium evolution reaction pathways in order to develop a simple model for loading, and we are able to obtain model parameters that can be fit to experiment.

#### 4. Modeling Cathodes with a High D/Pd Ratio

A motivation for our interest in the deuterium evolution reaction models is to understand better how loading works in the Fleischmann–Pons experiment. This is especially of interest in connection with the two loading requirements found over the years; one for a maximum achieved D/Pd loading of 0.95, and the other for a D/Pd loading greater than about 0.83 at the time excess heat is observed [4–7]. Our attention is then focused on the issue of how such high loading can be obtained. From the models discussed in the sections above we understand that deuterium is brought to the Pd cathode through the Volmer reaction, and that deuterium is lost to gas formation via the Tafel reaction. We understand that increasing the electrochemical current density is expected to produce more Volmer reactions, so that running at higher current density helps up until other processes come into play. However, we also understand that by loading we increase the chemical potential of the deuterium in the cathode, and this increases the rate at which D<sub>2</sub> gas leaves the cathode. In the Volmer–Tafel regime we are able to estimate the steady state loading from a balance between the two reactions.

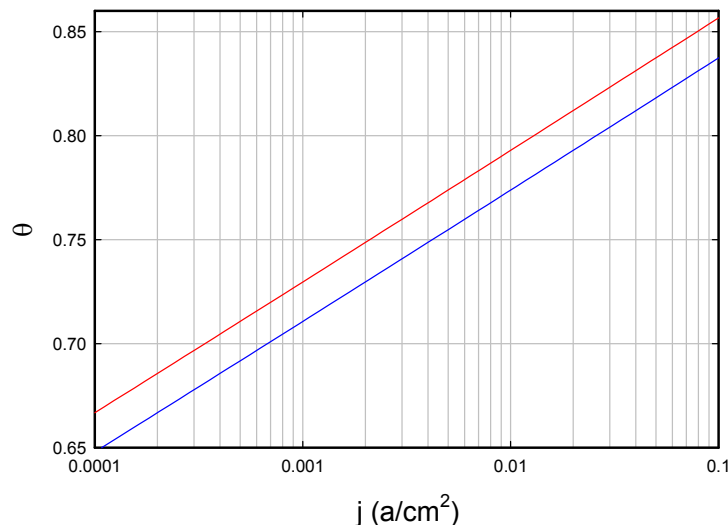
##### 4.1. Possible inconsistency with the model

But this is where we first run into a difficulty with the models. Our models as fit to the experimental data of Green and Britz [39] lead to an isotherm which in the complete absence of other processes predicts a maximum loading of  $\theta \leq 0.84$  at 100 mA/cm<sup>2</sup>. Presumably going to higher current density leads to a higher D/Pd ratio, but in the data of Green and Britz [39] we see that the increase is not going to be very much because the loading is saturating with increased current density. This effect is also seen in other experiments [38]. In essence, a version of the model that is fit to measurements on a cathode that does not load very well is going to predict a low loading in the Volmer–Tafel regime, and by extension will be inconsistent with cathodes that load more highly.

An immediate question that might be asked here is whether there experiments in which cathodes are observed to load better? If we peruse the literature, we can find many examples where cathodes achieve higher loading [47–53]. Moreover, in some of these experiments the cathodes are observed to achieve very high loading (above 0.90) at modest electrochemical current density consistent with the Volmer–Tafel regime (under 100 mA/cm<sup>2</sup>).

##### 4.2. Re-examination of the deuterium evolution reaction model

Consequently, this raises questions immediately about the basic deuterium evolution reaction models under discussion. If we imagined that the deuterium evolution reaction model were fundamental, then we might expect that the Volmer current model would describe the rate at which hydrogen loads through the Volmer reaction mechanism as a general statement, and similarly for the Tafel model. However, we now come to the conclusion that the models are not fundamental in this sense, simply because we need a new set of Volmer and Tafel fitting coefficients practically for



**Figure 7.** Volmer–Tafel isotherms for the basic model (blue line), and for a modified version of the model with a factor of 2 reduction in the Tafel prefactor (red line).

each cathode that loads to a greater or lesser degree. On the face of it this situation is either unacceptable, or perhaps much less useful than we might have hoped.

Now, we might suspect that there is a reasonably straightforward explanation for all of this. For example, it may be that at the heart of the problem is a minor variation in either the Volmer reaction prefactor (which we might explain by having either more or less active sites due to details of the surface orientation, or perhaps due to material deposited on the surface), or in the Tafel reaction prefactor (perhaps there are subtle differences in the surface which makes it either easier or harder for  $D_2$  molecules to form).

To test this, let us consider tweaking with the Tafel prefactor in order to see how much of a difference it makes for the loading in the Volmer–Tafel regime. For example, we can imagine that one surface might have a factor of two lower Tafel current density due to some subtle surface issues that might not be obvious upon inspection. In this case, we would expect the loading to increase with less gas loss. Perhaps we can reconcile the model in this way to account for the more highly loaded cathodes. A computation of the different Volmer–Tafel absorption isotherms shown in Fig. 7 in this case shows that we only achieve a relatively minor improvement in the loading. Certainly this is not going to be sufficient to account for cathodes that load much higher.

#### 4.3. Possibility of internal leaks

In studies that we pursued some years ago, we considered a number of different scenarios that were proposed to account for this problem. For example, if other species blocked surface sites, it is possible to reduce the Tafel current density more than the Volmer current density. However, this is not a particularly large effect unless most of the sites are blocked. Our conclusion was that if this were so, then one would see a difference in the overpotential between cathodes that load poorly and those that load well. We are not aware of such observations having been reported.

More likely in our view is a scenario in which a cathode that loads poorly does so because of internal leaks. We note that models for hydrogen and deuterium evolution are used most often in connection with cyclic voltammetry studies, in which the importance of the surface is emphasized. The use of a deuterium evolution reaction model to describe the bulk deuterium loading in steady state seems not to be so common. If we do model the bulk loading in this way, then we would naturally expect that deuterium loss through gas formation on internal surfaces would reduce the D/Pd loading. In this case we would want to modify the Tafel model to include contributions from internal leaks.

#### 4.4. Revised Tafel model to include internal leaks

We might then generalize the Tafel model to include internal leaks according to

$$j_T = r^2 j_{T0} \left( \frac{\theta}{\theta_0} \right)^2 e^{2(1-\delta_T)u(\theta-\theta_0)} + a j_{T0} \left( \frac{\theta}{\theta_0} \right)^2 e^{2(1-\delta_T)u(\theta-\theta_0)} + db, \quad (33)$$

where  $a$  is the ratio of the internal surface area to the outer geometric surface area. An earlier version of this kind of model was described in [30]. Such a formulation presumes that the  $j_{T0}$  prefactor then describes  $D_2$  gas formation as an idealized fundamental process, which acts the same (more or less) on internal surfaces as on the exterior surface. There are obvious reasons to argue that the prefactor for the internal surface could be somewhat different than for the external surface, for example due to the presence of the electrolyte on the external surface. However, our purpose here is to work with the simplest possible model that might be relevant to the problem.

#### 4.5. Determination of model factors

To proceed we require estimates for the factors that appear in the model. Presumably  $j_{T0}$  now refers to a more fundamental Tafel surface parameter, one which we cannot readily estimate from the data of Green and Britz [39]. However, if there were a cathode known to have no internal leaks, then we could parametrize the Tafel prefactor based on electrochemical data measured with the leak-free cathode. In recent years Pd cathode fabrication was studied at ENEA, and cathodes were optimized to produce high deuterium loading. One can see in the discussion of [56] that the grain size associated with some of these very good cathodes is on the order of the foil thickness. Under these conditions, one can imagine that the internal leaks are relatively small. It would of course be possible to work with metal samples with even larger grain size; however, such cathodes do not load particularly well.

In [51] is given some results for highly loaded cathodes where the loading was determined from resistance ratio measurements tabulated with the corresponding current densities. We see a number of cathodes that achieved very high loading at modest current density, with a loading of 0.93 reported at 80 mA/cm<sup>2</sup>, and 0.95 reported at 100 mA/cm<sup>2</sup>. Based on this it would seem that a value of the more fundamental version of  $j_{T0}$  in the range of

$$j_{T0} = 1.0 - 1.5 \times 10^{-6} \text{ A/cm}^2 \quad (34)$$

may be consistent. In these estimates we have kept a roughness factor  $r = 2$ .

#### 4.6. Internal leak rate

Once we have model parameters for the surface Tafel current, we can return to the question of the internal leak rate. For example, if we take  $j_{T0}$  to be  $10^{-6}$  A/cm<sup>2</sup>, then from the equivalent version of the fitting parameter found previously we would conclude that

$$4(1.69 \times 10^{-4}) = (4 + a)(1.0 \times 10^{-6}). \quad (35)$$

When this constraint is satisfied, the new model parameters will match our earlier fit for the Green and Britz [39] data. We can solve this to find

$$a = 672. \quad (36)$$

In light of this kind of model, we conclude that the cathode studied by Green and Britz [39] had an internal leak rate more than two orders of magnitude greater than the surface Tafel rate.

In our earlier work our estimate for  $\delta_T$  was lower, and our choice for a reference cathode was one which worked better than those listed in [51]. Consequently, our estimate for the ratio of the internal leak rate to the surface leak rate here is lower than the  $10^4$  estimate of [30]. We would benefit in this discussion by having available systematic electrochemical data taken with a cathode that achieves very high loading. For example, with data from an appropriate reference cathode, it may be that a reduction of an additional factor of 2–5 in  $j_{T0}$  could be argued for.

## 5. Summary and Conclusions

Many years ago John Bockris gave some talks about the Fleischmann–Pons effect in which he emphasized the importance of the Tafel curve. The prospect that it might be possible to develop models to describe cathode loading based on a solid electrochemical model was at the time inspiring. Now roughly a quarter of a century later, we know much more about the Fleischmann–Pons experiment; however, there remain many issues that still have not been resolved. Based on the literature, and based on the discussion in the preceding sections it seems clear that we should be able to have reliable models that we can use to understand the experiment. One of the most interesting questions has always been to understand what it is that is important in obtaining high loading.

In this work our focus has been on a subset of the deuterium evolution reaction model, focusing on the alkaline version of the Volmer reaction and the Tafel reaction. In steady state, we can develop a Volmer–Tafel adsorption isotherm to describe the adsorbed deuterium fraction on the surface. Purely for simplicity we have assumed that the surface sites and bulk sites are equivalent (the energies are known to be different), which allows us to extend the adsorption isotherm to serve as an absorption isotherm within the simple picture. This is interesting, as it allows us to compute the steady state cathode loading as a function of current density in the low current density Volmer–Tafel regime, and compare with experiment.

From a comparison with experiment we can develop model parameters simply enough, and when done we end up with a reasonable match. Unfortunately this simplest version of the model does not tell us how to achieve high loading, and seemingly we require a new version of the model for each cathode we are interested in. Ultimately we concluded that the resolution to this, in light of experiments with cathodes that show very high loading, is that there are internal leaks which are important and must be included in a bulk steady state absorption isotherm model. Moreover, these internal leaks constitute the dominant loss mechanism for deuterium from the cathode. In the case of the cathode studied by Green and Britz [39] we would conclude that the rate of deuterium loss through internal leaks is more than two orders of magnitude larger than the rate of deuterium loss from surface Tafel reactions.

We recall that immediately following the 1989 announcement of Fleischmann and Pons of the observation of excess heat in their electrochemical experiments, many researchers carried out versions of the experiment in attempts to replicate the experiment. Most of these efforts did not succeed. For many years we have been interested in understanding why. By now we are very familiar with D/Pd loading requirements that have been established as a prerequisite for observing excess heat [4–7]. The question that remains is why was there so much difficulty in obtaining the high

requisite loading. It is clear from the chemical potential that it is “hard” to obtain high loading, since the chemical potential increase needed over the miscibility gap is about 250 meV. For this one needs a moderately high current density, a clean system, but perhaps most importantly the cathode needs to be free of internal leaks. We conclude that a major factor contributing to the large number of failed experiments a quarter century ago was that the cathodes simply had large internal D<sub>2</sub> leaks. This conclusion is consistent with a point of view advocated often by McKubre over the past quarter century.

The discussion presented here constitutes the first part of a larger study that we carried out while on sabbatical at the Naval Postgraduate School some years ago. Additional issues that we looked at include other surface reactions, deuterium diffusion within the cathode, and dynamical loading calculations to compare with dynamical experimental data. We hope to publish additional results in the coming year.

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