

Research Article

Statistical Mechanics Models for PdH_x and PdD_x

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Abstract

In recent years we have developed simple empirical mean-field statistical mechanics models for PdH_x and PdD_x that include both O-site and T-site occupation. A brief account of this work is given here. At low loading it is impossible to fit solubility data over a wide range of temperature assuming only O-site occupation; however, with T-site occupation a good fit is obtained and an O-site to T-site excitation energy near 105 meV is found. Results from neutron diffraction studies at modest loading, and resistance and solubility measurements at high pressure and high loading, are used to infer O-site to T-site excitation energies and develop a smooth fit. The resulting statistical mechanics models have been optimized to provide systematic results at high loading for PdH and PdD, and also to fit the isotherms of the phase diagram of PdH. Estimates for the O-site energy as a function of loading and temperature have been developed in the latter case.

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Keywords: Mean field model, Palladium hydride, Phase diagram, Solubility, Tetrahedral occupation

1. Introduction

Since the announcement by Fleischmann and Pons of excess heat in the PdD system there has been interest among researchers interested in the effect to understand how it works. The problem is highly multi-disciplinary. A variety of issues that might be considered conventional are involved: electrochemical reactions that impact deuterium loading; diffusion of the deuterium within the cathode; the deuterium chemical potential and octahedral site occupation; physical chemistry and materials science issues at very high loading; and vacancy formation and occupation. Then there are issues that require new physics to understand, specifically concerning whatever physical processes are involved that enable nuclear energy to be expressed without commensurate energetic particles.

Over the last few years we have taken an interest in developing simple statistical mechanics models that describe the loading of hydrogen and deuterium in bulk palladium [1–3]. Such models can be useful for simulating cathode loading in the Fleischmann–Pons experiment; they can help in understanding what sites are occupied by interstitial H and D; the models can help interpret loading isotherms in terms of the energies of interstitial H/D states; and it may be possible to model what happens at high loading where the D/Pd ratio approaches or exceeds unity. In this short review

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we provide a brief overview of some of the results; a much more complete technical presentation of the models and how they were derived from statistical mechanics and experiment is provided in [1–3].

2. Modeling Solubility in the α -phase

Palladium hydride may be the most studied of the metal hydrides, both theoretically and experimentally. Near room temperature hydrogen and deuterium are known from experiment to occupy octahedral sites, a conclusion strongly supported by density functional and quantum chemistry calculations. Experimental solubility studies at low loading have been carried out over a wide range of temperatures, and theoretical models for hydrogen occupation of octahedral sites in alpha phase PdH_x have been available since the 1930s.

We focused on a data set published by Clewley et al. [4], which is of interest because it provides consistent data over a wide temperature range, and also because the results were provided in a form that is convenient to connect with theoretically. The data in this work is plotted as a function of

$$\frac{p(1-\theta)^2}{\theta^2}, \quad (1)$$

which is useful since according to Fowler and Smithells [5] one would expect in the α -phase an isotherm of the form

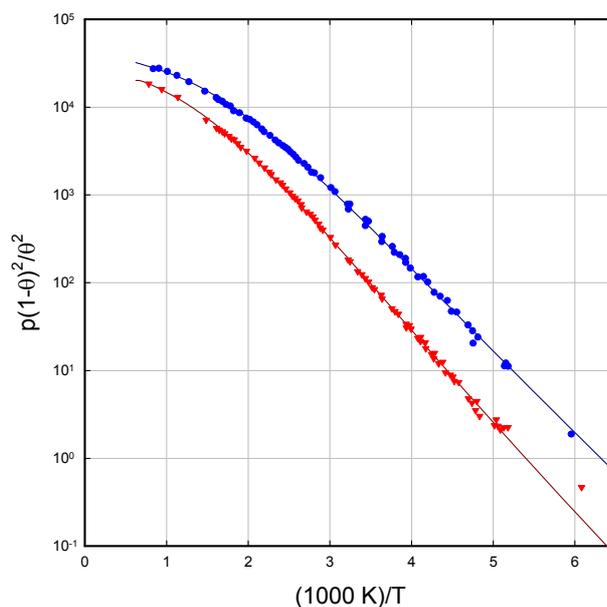


Figure 1. Plot of $p(1-\theta)^2/\theta^2$ for α -phase PdD_x as a function of $(1000 \text{ K})/T$ from [1]; data set of Clewley et al. [4] for PdH_x (red circles); optimized empirical model for PdH_x (red line); data set of Clewley et al. [4] for PdD_x (blue circles); optimized empirical model for PdD_x (blue line).

$$\frac{\theta}{1-\theta} = f(T)\sqrt{pe^{\Delta E/k_B T}} \quad (2)$$

if only octahedral occupation occurs in a model with constant ΔE . When plotted on a log-lin plot as a function of $1/T$ one would expect only minor deviations from a straight line due to the weak dependence of $f(T)$ on temperature; however, the data (see Fig. 1) shows a marked deviation from linearity at elevated temperature, which can be interpreted as resulting from the availability of (and occupation of) additional sites beyond the octahedral sites.

We found it to be impossible to develop acceptable fits to the data based on models for alpha phase PdH_x and PdD_x with O-site occupation alone; however, when we allowed for a combination of O-site and T-site occupation then good agreement could be obtained [1] as shown in Fig. 1. The O-site to T-site excitation energy derived from fitting the model with the data set was found to be 106.5 meV for PdH_x and 105.3 meV for PdD_x. Such a low energy excitation energy for T-site occupation was unexpected based on most of the relevant literature on solubility; however, recent modeling with density functional theory codes and quantum chemistry codes is qualitatively consistent with these results.

3. O-site to T-site Excitation Energy

The low O-site to T-site excitation energy at low loading would suggest that T-site occupation might be important at higher loading. Although there are many computations of the excitation energy from density functional calculations and from quantum chemistry calculations, there has not been any previous systematic effort to connect the results with experimental solubility studies. There have been arguments made in the literature where it was suggested that information about the excitation energy could be obtained from estimates for the barrier energy associated with H or D diffusion in Pd; for α -phase PdH_x at low temperature the barrier energy is listed as 0.13 eV [6], which is a bit higher than our estimate derived from the α -phase solubility. The barrier energy near room temperature for the α -phase is higher, for PdD the barrier energy is listed as 0.206 meV [6], perhaps indicative of the participation of higher energy states (see [7]). For β -phase PdH Baranowski provides a fit dependent on temperature with a corresponding barrier energy of 281 meV [8].

We would conclude from this that the O-site to T-site excitation energy is probably less than 280 meV near an H/Pd loading of 0.6. However, we require a parameterization of the O-site to T-site excitation energy in order to implement a statistical mechanics model for H/D solubility in Pd above the α -phase. We made use of solubility data at high loading and quasi-elastic neutron scattering studies at lower loading to construct an empirical estimate for the O-site to T-site excitation energy as a function loading shown in Fig. 2 (as discussed in detail in [2]). Here we give only a brief outline of the approach. The analysis of the α -phase region outlined above provides an estimate at zero loading. We applied the same statistical mechanics model to all available solubility data at high loading [2], including solubility data indicative of above unity D/Pd loading published by Baranowski [9]. We found that it was possible to estimate the excitation energy by matching the model to the change of slope in the resistance ratio data at high pressure, and that the resulting model was consistent with other high pressure data as well as with the resistance ratio calibrations of Crouch-Baker et al. [10]. The resulting excitation energies for both PdH and PdD at a loading of unity was estimated to be about 225 meV (shown in Fig. 2). There are a small number of neutron diffraction experiments, such as the study of Pitt and Gray [11], which can be interpreted in terms of T-site occupation. In Ref. [2] the data was analyzed to give the (inferred) data points shown in green between about $\theta = 0.08$ and $\theta = 0.42$.

A parameterization for PdD_x was developed based on a least squares fit of the data points shown to

$$\Delta E(\theta) = \frac{\alpha_0 + \alpha_1\theta}{1 + \beta\theta} \quad (3)$$

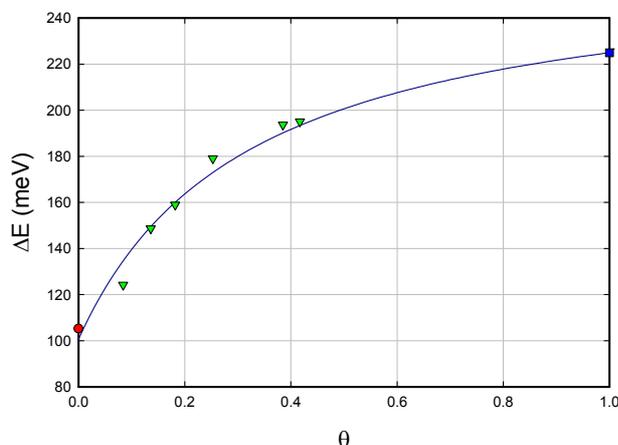


Figure 2. O-site to T-site excitation energy as a function of loading [2]; inferred from data of Pitt and Gray [11] (*green triangles*); estimated from high pressure loading data of Baranowski et al. [9] (*blue square*); excitation energy from α -phase PdD_x analysis of [1] (*red circle*); empirical fit (*dark blue line*).

resulting in the fitting parameters

$$\alpha_0 = 100.676 \text{ meV}, \quad \alpha_1 = 824.259 \text{ meV K}^{-1},$$

$$\beta = 3.1108 \text{ K}^{-1}. \quad (4)$$

The resulting fit can be seen in Fig. 2. We had not anticipated the apparent consistency between the O-site to T-site excitation energy from the analysis of data from such disparate sources. Also, we were expecting to find the excitation energies for PdH and PdD to be different by on the order of 10–20 meV; it came as a surprise that very similar results were obtained near $\theta = 0$ and $\theta = 1$. It is probable that the O-site to T-site excitation energy is also a (weak) function of temperature; but at this point there is insufficient data available to develop a parameterization that takes into account both loading and temperature.

4. Solubility at High Loading

Models in the literature based on O-site loading predict an upper limit for the H/Pd or D/Pd ratio of unity, as would be expected if there are no other sites that could be occupied. As mentioned above Baranowski [9] reported high pressure experiments with PdD in which it was concluded that a D/Pd loading higher than unity had been developed. In electrochemical studies with PdD in our field there have been claims that a D/Pd ratio greater than unity have been obtained. This presents no particular difficulty if T-site occupation occurs (or if a different phase is present), but is problematic in models with only O-site occupation.

It is possible to make use of the Sarkur–Tetrode chemical potential of the ideal gas law for the development of statistical mechanics model at low pressure and loading; however at high loading the equivalent pressure can be as large as 1 GPa, where hydrogen deviates significantly from an ideal gas. This provided us with motivation to examine

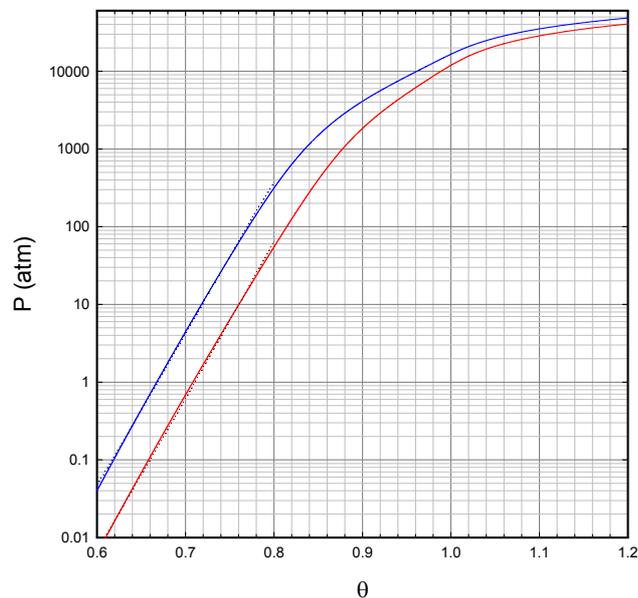


Figure 3. Model pressure as a function of loading θ at 300 K [2]; PdH (red line); low-pressure empirical model of Baranowski et al. [9] for PdH (dark red dotted line); PdD (blue line); low-pressure empirical model of Baranowski et al. [9] for PdD (dark blue dotted line).

models for the fugacity of H_2 and of D_2 gas [12]. We concluded that the difference between the best of the recent fugacity models for H_2 and D_2 was much greater at high loading than would be expected from the equation of state (even so the differences are small), so that it would be appropriate to make use of the H_2 fugacity to model D_2 . We are able to get reasonably good agreement with the high pressure loading data using a model that includes both O-site and T-site occupation, taking advantage of the O-site to T-site excitation models discussed above; the model pressure composition isotherms that result for PdH_x and PdD_x are shown in Fig. 3 [2].

5. Phase Boundary Near a Loading of Unity

Reviewers for this paper and previous papers have raised the issue of the absence of an obvious phase boundary between the β -phase below $\theta = 1$ and a tetrahedral phase above $\theta = 1$. We were expecting to see a discontinuity around $\theta = 1$ in the isotherm, perhaps with a factor of two or three increase in pressure required to proceed past $\theta = 1$. Some of the early models that we explored in which a large O-site to T-site excitation energy was assumed showed exactly such an effect. However, when we made use of all available high pressure solubility data, it became clear that the excitation energy was relatively low (225 meV is not a particularly large excitation energy in this context), and that the transition from the β -phase to the T-site phase in the model was gentle. The O-site and T-site fractional occupation from the models are shown in Fig. 4 [2].

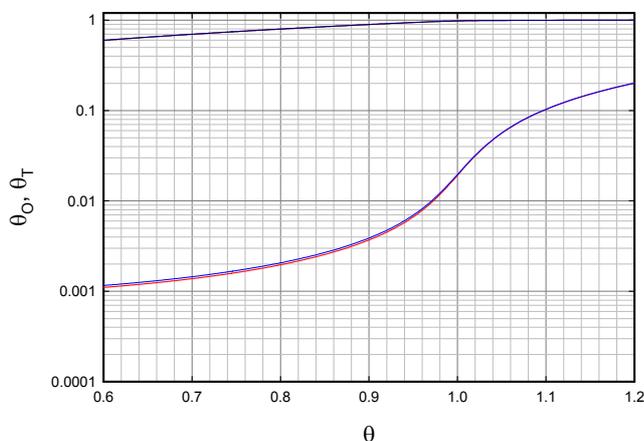


Figure 4. O-site fraction for PdH (*upper dark red line, under upper dark blue line*) as a function of θ ; T-site fraction for PdH (*lower red line*); O-site fraction for PdD (*upper dark blue line*); T-site fraction for PdD (*lower blue line*).

6. Modeling the Phase Diagram

We were interested in the possibility of applying the simple statistical mechanics models with both O-site and T-site occupation to model the isotherms of the phase diagram. Since these isotherms involve different data sets and also different temperatures, we thought that it might be possible to check for consistency with our model for the O-site to T-site excitation energy. In addition, we were interested in developing estimates for the O-site energy as a function of loading and temperature, which would only be possible if fitting were done starting at low loading. We found that a good fit was possible if we made use of the O-site to T-site excitation energy from the earlier study (shown in Fig. 2) [3]; the resulting fitted isotherms are shown in Fig. 5. The O-site energies consistent with this phase diagram are illustrated in Fig. 6. The optimization of the phase diagram fit in the case of no T-site occupation leads to unphysical results for the O-site energy curves (the mean O-site energy decreases with temperature at some loadings, which is inconsistent with a simple configuration splitting of the O-site energies). If we fit with a model that optimizes the O-site to T-site excitation energy, then we end up with a very good mathematical fit to the phase diagram but once again the resulting O-site energies are unphysical.

Note that according to this model, the energy of H in PdH_x is lower than in H₂ at all loadings. This will also be true for the energy of D in PdD_x, which is not in agreement from the conclusion derived from the enthalpy curves widely used in the literature.

7. Summary and Discussion

It has long been taken as settled that the solubility of PdH_x and PdD_x can be accounted for with interstitial hydrogen/deuterium in octahedral sites. This is consistent with early theoretical models, and also with early neutron scattering studies of PdD. However, we found it impossible to account for the solubility data of Clewley et al. with such models. It was only when we allowed for T-site occupation that good agreement could be obtained, with a relatively low O-site to T-site excitation energy near 105 meV. Quasi-elastic neutron diffraction studies of PdD_x at elevated temperature showed peaks consistent with T-site occupation which is supportive of this approach, and which provides

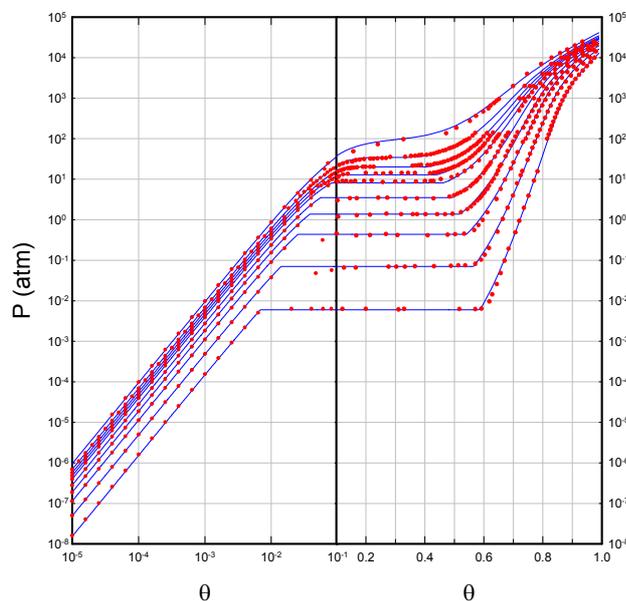


Figure 5. Isotherms and data points for the model with temperature-dependent 6th-order polynomial fit of E_O and an empirical ΔE model, from [3]. The isotherms from low to high are for temperatures of 20, 70, 120, 160, 200, 243, 270, 300, 340, and 433°C.

estimates for the O-site to T-site excitation energy at intermediate loading. At high pressure there are some solubility studies which allow for an estimate of the excitation energy, and we found it possible to obtain agreement between the models and experimental data with an excitation energy near 225 meV. We made use of the statistical models for O-site and T-site occupation to model the phase diagram of PdH_x , and found good agreement when we made use of our empirical model for the O-site to T-site excitation energy with temperature-dependent O-site energies that are physically plausible.

In view of the DFT calculations of Yoshinari [7], a mean field model based on O-site and T-site occupation constitutes a significant simplification of a complicated situation. For example, one might imagine some time in the future where DFT computations for PdH_x become accurate at the meV level; in this case a better statistical mechanics model could be developed based on the occupation of O-sites on the same footing with the different excited states systematically. Perhaps such a model would be able to predict solubility as well as diffusion coefficients from the same more general formulation. Such a project seems well beyond our capability today, which is why the much simpler O-site and T-site mean field model we have developed may be useful at the present time.

In the future we would like to make use of the approach outlined in this paper to develop a mean-field statistical mechanics model for palladium deuteride. Our hope is that these models might stimulate new experiments that can address the issue of T-site occupation, so that we might have more confidence in our understanding of these systems. We are also interested in pursuing modeling of the NiH system, due to its importance in Condensed Matter Nuclear Science.

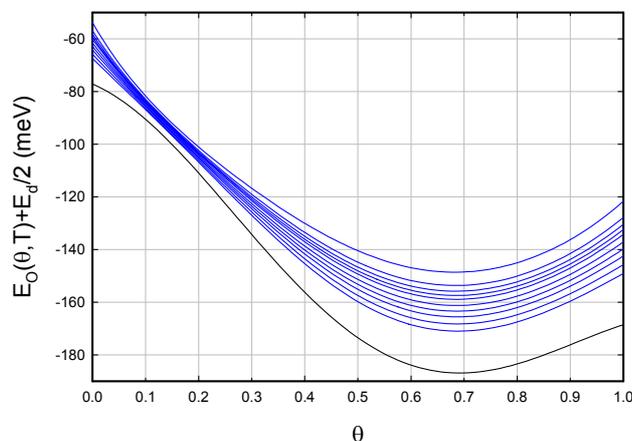


Figure 6. O-site energies as a function of loading from Ref. [3] for the different temperatures (20, 70, 120, 160, 200, 243, 270, 300, 340, and 433°C) of the isotherms of Fig. 4 (blue lines); extrapolation to $T = 0$ (black line).

Appendix A. Discussion on Points Raised by the Reviewer

The reviewer has raised a number of issues which we consider in this Appendix.

Appendix A.1. Possible phases at high loading

The reviewer has written:

Apparently the reviewer and the author have a basic difference in how they interpret the behavior of crystal structures such as that of PdD. Generally, structures of atoms tend to change from one form to another rather than have the atoms move into tetrahedral sites, which requires high energy. For example, in the Zr–H system, the cubic form of ZrH converts to a tetrahedral form designated ZrH₂ when sufficient H₂ pressure is applied. Presumably the same transformation might occur in the Pd–H system, which the author notes.

Evidence summarized by Storms in [14] shows a limit to the cubic phase near but slightly less than PdH₁. A H/Pd ratio greater than this value would presumably be a mixture of cubic PdH and tetragonal PdH₂. Although this conclusion has not been proven, it at least needs to be acknowledged when discussing the possibility of tetrahedral occupancy and its influence on the limit of the cubic phase.

To understand what crystal structures are present at a D/Pd loading above unity it will be necessary to do X-ray diffraction in order to determine the Pd substructure, and neutron diffraction to determine the D substructure. Until unambiguous measurements are done that settle the issue, it is clear that people will continue to make spirited cases for one structure or another. Certainly the modeling the the author has carried out is not intended as a substitute for such much needed experiments.

The author is of the opinion that the Fukai structure is thermodynamically preferred at a loading above about PdD_{0.95} near room temperature. Near room temperature atomic self-diffusion of Pd atoms is slow, so that it might

take a large number of years for superabundant vacancies to form in large amounts. If so, then it may be that the Pd sublattice remains FCC, and interstitial H or D fills O-sites first and then more highly excited states subsequently. This is presumed in the model under discussion in this paper.

In most DFT and in other simulations H is found to occupy O-sites as the lowest energy available sites. Certainly there are excited orbitals available [7], which the T-site is an example. The model discussed in the paper adopts a simplistic picture of an O-site and a T-site as anharmonic wells, which is useful in the sense that there is additional freedom within the model to connect with experimental data quantitatively. It would certainly be possible to develop better statistical models that take advantage of more realistic excited state energies once they are known, and also to take account of more accurate many-body energies associated with the various configurations once reliable estimates become available. If and when the crystal structure in the vicinity of unity loading and above is clarified, there will be no problem developing statistical models that take into account a different crystal structure and interstitial state energies.

Appendix A.2. Role of tetrahedral occupation

The reviewer has written:

Based on previous papers, the author apparently is intent on showing how D can occupy tetrahedral sites as the location of the LENR fusion reaction. Although this is a worthy goal, the conclusions must also be consistent with the conventional behavior of PdD. This reviewer is only asking that this consistency, or lack thereof, be acknowledged. The author concludes that inclusion of tetrahedral occupancy provides a better fit to the available data. While this might be true, the reviewer would like to have this conclusion made more obvious.

The initial goal associated with the various studies summarized in this paper was to see whether a statistical model could be developed that might be relevant to D/Pd loading near and above unity. The large majority of statistical models in the literature are simply not applicable to the case of interstitial loading above unity, primarily because they are restricted to O-site occupation. In this sense the research was exploratory.

However, once work started in earnest on this kind of model it became possible to make a connection with many experimental measurements. As discussed above, it is impossible to account for alpha-phase solubility data with a mean-field model based only on O-site occupation (with either harmonic or anharmonic potentials). The neutron diffraction data at modest loading implicates T-site occupation (which the author was not aware of during the initial development of the model). And it was possible within the model to develop fits which connected with experimental data near and above unity loading. Of course analogous statistical models can be developed based on other schemes and crystal structures that would similarly be able to connect with experimental data sets at high loading – there is nothing unique in this sense about the model under discussion in this paper.

The hope was to develop a statistical model that might be used systematically over the different regions, including low and high loading, as well as low and high temperatures. If we would like to develop a reasonably general simulation model for the Fleischmann–Pons and related experiments, such a model would be extremely helpful.

It was never the case, as the reviewer suggests, that the tetrahedral site in bulk PdD was considered by the author as the site for any LENR fusion reaction. As has been discussed a great many times [13], this author considers monovacancies (or their equivalent in the Fukai structure) to be where deuteron-deuteron reactions occur in the F–P experiment.

Appendix A.3. Isotherm of Santandra and Behrens

The reviewer has written:

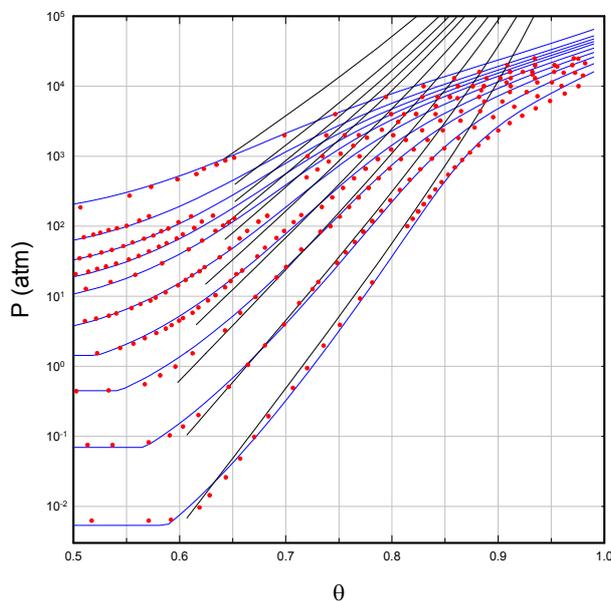


Figure 7. Close-up of data points (red circles) and model isotherms (blue lines) from Fig. 5 displayed with isotherms from the Santandrea and Behrens parameterization (black lines).

Santandrea and Behrens [15] give the following equations as their description of the H_2 pressure in equilibrium with β -PdH based on the data available at the time.

$$P(H_2) = \exp\left(-\frac{4693}{T} + 10.97\right), \quad \text{miscibility gap,}$$

$$P(H_2) = \exp\left(12.9 + 2 \ln \frac{\theta}{1-\theta} - \frac{12070 - 10830 \theta}{T}\right), \quad \beta\text{-PdH.}$$

How do these equations compare to the equations the author obtains using his treatment? Can the author provide a better fit to all available data based on his approach? If so, please provide equations showing the effect of pressure in a form that can be used by an experimenter.

Perhaps the place to start might be to compare the isotherm of Santandrea and Behrens in the beta phase with the set of PCT points that we used, and with our model isotherms. The results are shown in Fig. 7. One sees that the Santander and Behrens fit works best near room temperature and at modest pressures (we found a similar restriction in applicable range in Baranowski's parameterization). Our model is discussed in detail in [3].

References

- [1] P.L. Hagelstein, O-site and T-site occupation of α -phase PdH_x and PdD_x , *J. Condensed Matter Nucl. Sci.* **17** (2015) 67–90.

- [2] P.L. Hagelstein, Empirical models for octahedral and tetrahedral occupation in PdH and in PdD at high loading, *J. Condensed Matter Nucl. Sci.* **17** (2015) 35–66.
- [3] P.L. Hagelstein, Models for the phase diagram of palladium hydride including O-site and T-site occupation, *J. Condensed Matter Nucl. Sci.* **20** (2016) 54–80.
- [4] J.D. Clewley, T. Curran, T. B. Flanagan and W. A. Oates, Thermodynamic properties of hydrogen and deuterium dissolved in palladium at low concentrations over a wide temperature range, *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases* **69** 449–458 (1973)
- [5] R. H. Fowler and C.J. Smithells, A theoretical formula for the solubility of hydrogen in metals, *Proc. Roy. Soc. London, Series A, Math. Phys. Sci.* **160** 37–47 (1937).
- [6] Y. Fukai, *The Metal–Hydrogen System*, Springer, New York, 1993.
- [7] O. Yoshinari, Origin of ‘Inverse Isotope Effect’ of hydrogen diffusion in palladium, In *Defect and Diffusion Forum* **312** (2011) 295–300.
- [8] S. Majorowski and B. Baranowski, Anomalous behavior of diffusion coefficients of hydrogen and deuterium in high content palladium hydride and deuteride, *Electronic Structure and Properties of Hydrogen in Metals*, Plenum Press, New York, 1983, pp. 519–524.
- [9] B. Baranowski, S. M. Filipek, M. Szustakowski, J. Farny and W. Woryna, Search for “cold-fusion” in some Me–D systems at high pressures of gaseous deuterium, *J. Less Common Metals* **158** (1990) 347–357.
- [10] S. Crouch-Baker, M.C.H. McKubre and F.L. Tanzella, Variation of resistance with composition in the β -phase of the H–Pd system at 298 K, *Zeitschrift für Physikalische Chemie* **204** (1998) 247–254.
- [11] M.P. Pitt and E.M. Gray, Tetrahedral occupancy in the Pd–D system observed by in situ neutron powder diffraction, *Europhys. Lett.* **64** (2003) 344.
- [12] P.L. Hagelstein, Equation of state and fugacity models for H₂ and for D₂ *J. Condensed Matter Nucl. Sci.* **16** (2015) 23–45.
- [13] P.L. Hagelstein, Current status of the theory and modeling effort based on fractionation, *J. Condensed Matter Nucl. Sci.* **19** (2016) 98–109.
- [14] E.K. Storms, *The explanation of low energy nuclear reaction*, Infinite Energy Press, Concord, NH, 2014, pp. 127–128.
- [15] R.P. Santandrea and R.G. Behrens, A review of the thermodynamics and phase relationships in the palladium–hydrogen, palladium–deuterium and palladium–tritium systems, *High Temperature Materials and Processes* **7** (1986) 149.