

Some Thermodynamic Properties of the H(D)-Pd system

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Abstract

In any discussion of the origin, measurement or description of the anomalous power producing process which occurs in connection with the electrochemical loading of deuterium into palladium, knowledge of the thermodynamic behaviour of the system is clearly of importance. More particularly, since the formation of highly loaded palladium is implicated as a necessary (but itself insufficient) condition for the observation of anomalous power, thermodynamic considerations relating to the attainment of high loadings are of interest. Here, it is intended to review, at a general level, those aspects of the thermodynamic nature of the H(D)-Pd system, both equilibrium and non-equilibrium, which appear to bear most directly on the question of excess power production in relation to the attainment of high loadings.

1. Introduction

Although considerable effort has been expended in the study of the H(D)-Pd system,^{1,2} relatively little attention has been paid to the thermodynamic properties of compositions within the β (α') phase, in particular for $x > 0.8$. In the context of excess power production in the D-Pd system, this deficiency is particularly unfortunate since the attainment of loadings higher than about 0.85 appears to be *one* of the criteria necessary for its observation.³⁻⁶

Experimentally, the reproducible attainment and maintenance of electrochemical loadings larger than about 0.85 have proven to be more challenging than might be expected from cursory inspection of earlier literature and, presently, much of the effort in the "new hydrogen energy" field is devoted to this issue. Clearly, in order to understand fully the calorimetric behaviour of the H(D)-Pd system at elevated loadings (i.e. elevated values of the H(D) *chemical potential*, at modest temperatures and pressures³), a number of thermodynamic issues must be addressed. A number of such issues are discussed briefly here; although both hydrogen and deuterium alloys are described, the data cited are for H-Pd (at 298 K) unless otherwise indicated.

2. Non-ideality in the H(D)-Pd system

Any description of the thermodynamic properties of the β phase must take into account the fact that it is a non-ideal solution of hydrogen in palladium. Thus the thermodynamic state functions vary not only with temperature and pressure (or

volume), but also with *composition*. The chemical potential of hydrogen in palladium may be written as:⁷

$$\mu = \mu^0 + R T \ln \frac{x}{1-x} + \mu^{\text{ex}} \quad (1)$$

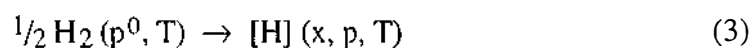
where the term μ^{ex} is introduced to account for deviations from ideal solution behaviour. For didactic purposes at least, it is found convenient to regard the dissolved hydrogen as electronically screened protons. This leads to the decomposition of μ^{ex} into two (additive) terms: Firstly, an “elastic” term due to the dilation of the lattice on occupation by hydrogen. This term is increasingly negative with increasing x (very approximately linearly so) corresponding to a net attractive interaction between the screened protons. Secondly, an “electronic” term which reflects the rise in the Fermi level due to the electrons associated with the dissolved hydrogen. This term is increasingly positive with increasing x , increasing relatively slowly for $x < 0.6$ as the high density-of-states 4d band is occupied, but more rapidly, and approximately linearly, at higher loadings as electrons are forced to enter the low density-of-states 5s band (for a detailed account, see Ref. 2). For compositions in the β phase ($x > 0.6$) the electronic term dominates, leading to a linear variation of μ with x , as has been observed experimentally for both H and D, at least up to $x = 0.8$.^{8,9}

The non-ideal nature of hydrogen in palladium has several consequences of interest in the context of loading. For example, the dependence of chemical potential on loading contributes directly to the Fick’s law diffusion coefficient,

$$D_F = M x \frac{\partial \mu}{\partial x} \quad (2)$$

Recent measurements on the H-Pd system reveal that D_F increases with x in the β phase¹⁰ indicating that the rapid rise of μ with loading offsets the anticipated drop in mobility with increased octahedral site occupancy (however, contrary data have been reported¹¹).

Another quantity of interest is the (relative) partial molar enthalpy of absorption in the β phase, ΔH_T . This is the enthalpy change for the *constant temperature* process



By considering ΔH_T to be a function of volume and composition, we may derive the following compositional dependence^{2,12}

$$\Delta H_T = \Delta H_T(x=0) - \frac{V_{\text{H}}^2 K x}{V_{\text{Pd}}} + \int_0^x \left(\frac{\partial \Delta H_T}{\partial x} \right)_V dx \quad (4)$$

The second and third terms on the right-hand-side of Eqn. 4 behave analogously to the elastic and electronic contributions, respectively, to the chemical potential. In Fig. 1, the quantity “ $\Delta H_T - \Delta H_T(x=0) - p V_{\text{H}}$ ” is plotted schematically versus loading, together with its “elastic” and “electronic” components.¹³ (Qualitatively, the behaviour of this

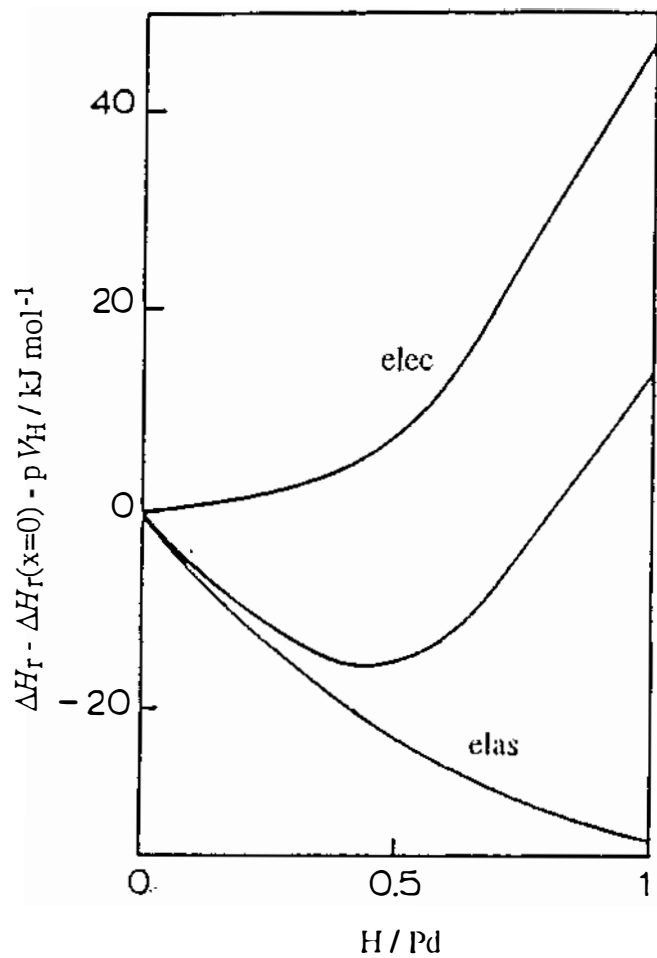


Figure 1. Compositional dependence of elastic and electronic contributions to relative partial molar enthalpy. Adapted from Ref. 13.

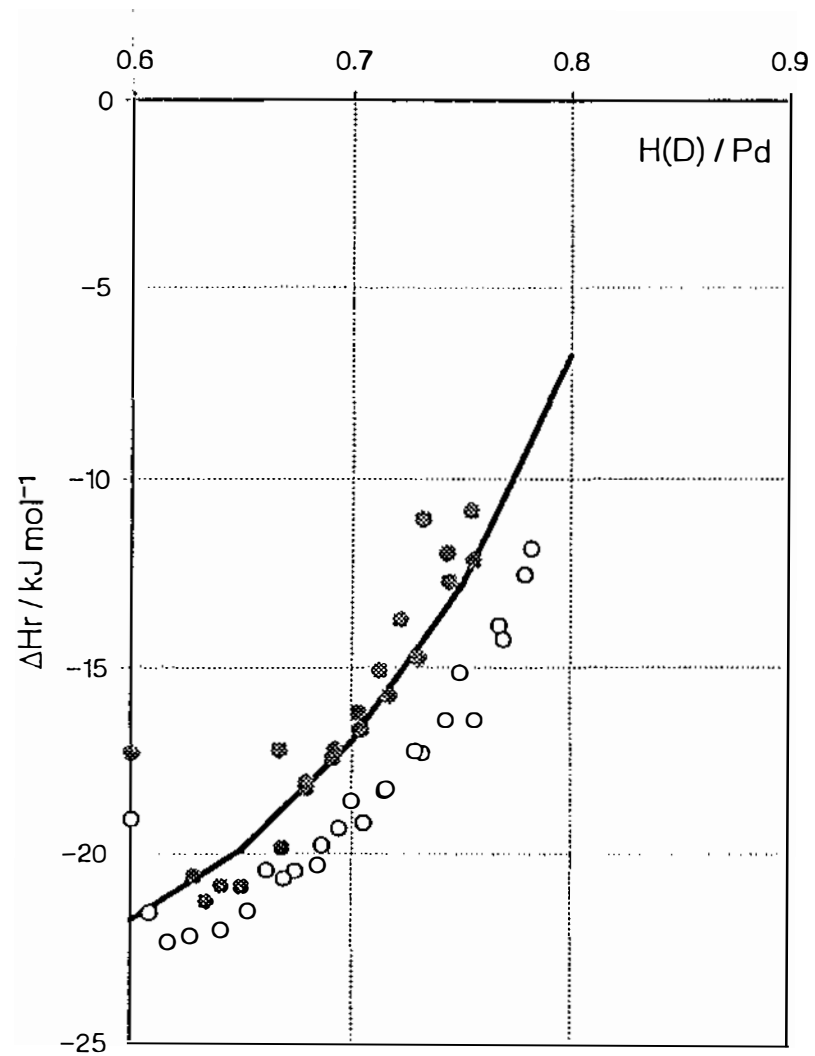


Figure 2. Relative partial molar enthalpies: calorimetrically determined, H (open circles), D (filled circles); calculated, H (line). Data from Refs. 9 and 14.

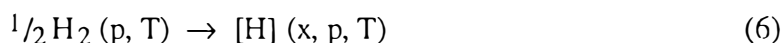
quantity is the same as that of ΔH_T itself since the additional terms are either relatively small or constant). At low loadings, the partial molar enthalpy of absorption is exothermic, due to the dominance of the negative elastic contribution. However, similar to the behaviour of the chemical potential, in the β phase region the electronic term dominates, causing the relative partial molar enthalpy to become more positive with increasing loading. The results of a detailed statistical thermodynamical calculation of ΔH_T for *hydrogen* are shown in Fig. 2.¹⁴ It is apparent that, unless a phase change occurs in the region $0.8 < x < 1.0$, ΔH_T is expected to become endothermic somewhere in this interval. In Figs. 1 and 2, it should be noted that the existence of the two-phase region for $x < 0.6$ has not been explicitly recognized; this is often the case in modelling studies based on equations such as (1) and (4). For increasing loading in the two-phase region, the molar enthalpy change is independent of composition and approximately -19 kJ mol^{-1} for H-Pd and -17 kJ mol^{-1} for D-Pd.⁹

Calorimetrically measured values of ΔH_T are shown for both hydrogen and deuterium in Fig. 2.^{9,15} Although these data do not extend to particularly high loadings, they are in broad, if not exact, agreement with theoretical predictions. It is of interest to note that the exothermic / endothermic transition is expected to occur at a lower loading for deuterium than for hydrogen. It should be remarked that experimental values of ΔH_T are available in the literature for $x > 0.9$.¹⁶ However, other researchers have questioned these data¹⁷ and they are not included here.

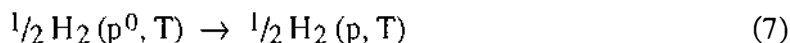
Since direct calorimetric measurement of ΔH_T at high x may be difficult, it is of interest to see if other experimental data may be used to derive ΔH_T values. From elementary thermodynamics we may derive

$$\Delta H_T = T (V_H - 1/2 V_{H_2}) \left(\frac{\partial p}{\partial T} \right)_x - \frac{R T^2}{2} \left(\frac{\partial \ln f_{H_2}}{\partial T} \right)_p \quad (5)$$

where the first term on the right-hand-side is the partial molar enthalpy change for the process



This is a negative quantity at accessible pressures. The second term corresponds to the molar enthalpy change (a positive quantity) for the process



This latter process is well-characterised thermodynamically; thus calculation of ΔH_T is essentially a matter of determining the pressure-compositions isotherms over a range of temperatures at high loadings.

For a finite change in loading at constant temperature (involving the production or consumption of hydrogen gas at 1 atm.), the total enthalpy change is given by

$$\Delta H(x_1 \rightarrow x_2) = \frac{1}{x_2 - x_1} \int_{x_1}^{x_2} \Delta H_T dx \quad (8)$$

Furthermore, the total energy change, $\Delta U(x_1 \rightarrow x_2)$, and $\Delta H(x_1 \rightarrow x_2)$ differ by no more than about 1 kJ mol^{-1} , for loadings up to approximately unity.

3. Gas-phase vs. electrochemical loading

Gas-phase and electrochemical loading differ thermodynamically in two important respects: Firstly, with respect to the value of μ for a given loading; secondly, with respect to the ease of measurement of μ (and, hence, the loading) for each loading method. In what follows, it is assumed that metallurgical considerations do not intervene to lower the loading below that (maximum) value which corresponds to the thermodynamic state of surface adsorbed hydrogen atoms, i.e. in the electrochemical steady-state, the metal is internally in equilibrium. Furthermore, for ease of expression, only acidic conditions are considered in the electrochemical case; the following arguments are unchanged for loading in basic solutions. Finally, during electrochemical loading, it is assumed that the ambient hydrogen pressure is 1 atm.

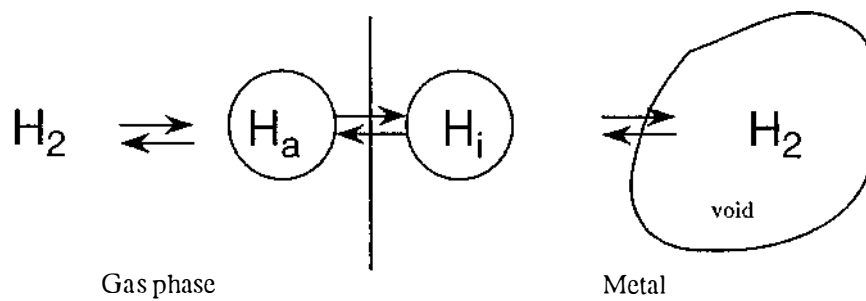
The essential differences between gas-phase and electrochemical loading are illustrated in Fig. 3. In this figure, H_a represents a surface-adsorbed hydrogen atom, while H_i represents dissolved hydrogen. In gas-phase loading, a state may be reached where the enviroing hydrogen gas, surface adsorbed hydrogen atoms, dissolved hydrogen atoms and any hydrogen gas formed in voids within the metal are in equilibrium. In this case, the loading at a given temperature is determined by the fugacity of the enviroing hydrogen gas (or hydrogen partial pressure, at pressures less than about 100 atm.). In the electrochemical case, on the other hand, the steady-state does not necessarily correspond to equilibrium between the enviroing hydrogen gas and the surface adsorbed hydrogen atoms. Hence, the sample experiences a hydrostatic pressure of 1 atm. regardless of the chemical potential of surface adsorbed hydrogen atoms. (Note, however, that any gas formed in voids within the metal is in chemical equilibrium with the dissolved hydrogen, leading to pressurized voids). Thus, *at a given loading*, the chemical potential of dissolved hydrogen loaded electrochemically, $\mu(p^0, x)$, is related to the chemical potential obtained in gas-phase loading, $\mu(p, x)$, by

$$\mu(p^0, x) = \mu(p, x) - \int_{p^0}^p V_H dp \quad (9)$$

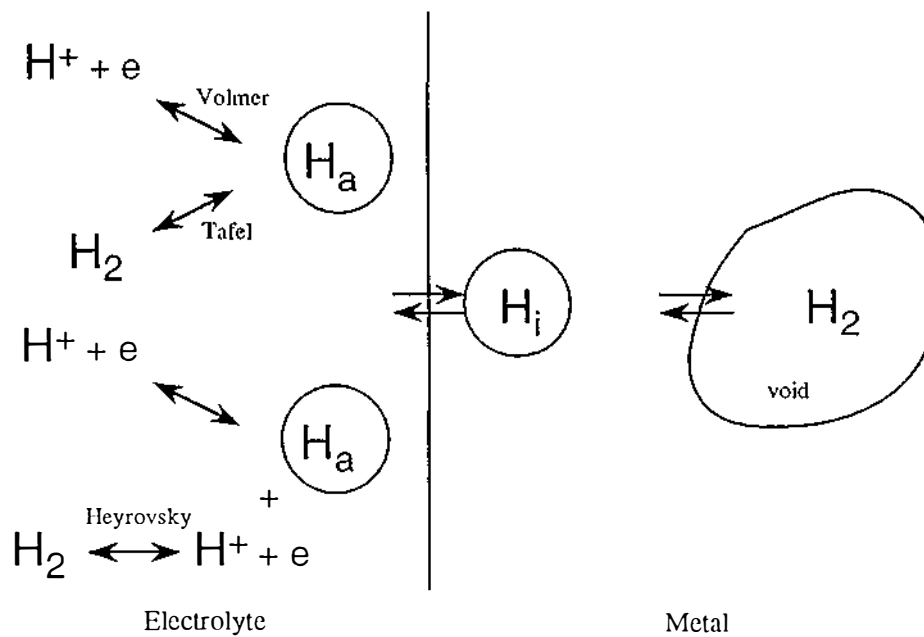
This difference, although conceptually important, is generally small numerically. In other words, those physical properties of gas-loaded and electrochemically loaded palladium which are dependent of the chemical potential of hydrogen will differ only negligibly; for example, the pressure generated within voids in the metal when loaded electrochemically will be slightly less than that generated under gas-phase loading, for the same loading. As an aside, we note that a situation similar to electrochemical loading exists in so-called *gas phase atomic loading*, Fig. 3. Here, hydrogen atoms are generated continually in the gas phase from molecular hydrogen using a hot wire. These hydrogen atoms are not equilibrated with the molecular hydrogen, i.e. are formed with an elevated chemical potential, and are thus capable of causing high loadings, as has been demonstrated experimentally.¹⁸ We speculate that the ultrasonic cavitation of water in the presence of a palladium substrate (where hydrogen atom generation is known to occur¹⁹) will have similar consequences.

The following question naturally arises: can we, in an electrochemical experiment, infer the loading of a palladium cathode from the measured cathode

a) Gas phase loading - chemical equilibrium



b) Electrochemical loading - steady-state



c) Gas phase atomic loading - steady state

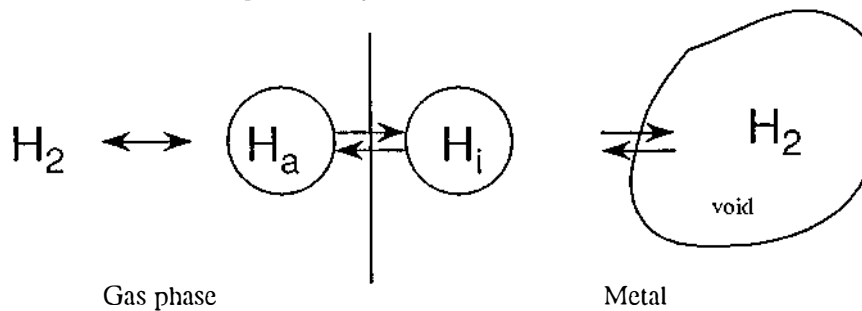


Figure 3. Loading mechanisms

overvoltage? In gas-phase loading, knowledge of the hydrogen pressure and the temperature are sufficient to determine the palladium loading at equilibrium. Thus gas-phase loading is generally not suitable for achieving very high loadings due to the experimental difficulties caused by the enormous pressures involved. In electrochemical loading, on the other hand, while it is possible to generate overvoltages at a palladium cathode which are, in principle, sufficient to raise the chemical potential of the dissolved hydrogen to values necessary for loadings approaching unity (greater than 35 kJ mol^{-1} or 0.35 eV for H), it is *not* possible to convert a measured overvoltage directly into a loading without detailed knowledge of the electrochemical reaction mechanism. This subject has been discussed extensively in the literature²⁰⁻²³ and only the key points are summarized here.

In general, two *extreme* cases may be recognized:

(i) For an electrochemical reaction in which the electron transfer (Volmer) step has a relatively small - in the limit, zero - affinity (i.e. is in a state of “quasi-equilibrium”):

- The dissolved hydrogen is not equilibrated with the envioning hydrogen.
- High loadings are possible (the chemical potential of dissolved hydrogen is directly proportional to the (negative) overvoltage measured with respect to a standard hydrogen reference electrode, η).
- Metal voids are pressurized, leading potentially to cracking and blistering.

(ii) For an electrochemical reaction in which the hydrogen atom recombination (Tafel) step is in quasi-equilibrium:

- The dissolved hydrogen is equilibrated with the envioning hydrogen.
- High loadings are not possible (the chemical potential of dissolved hydrogen is given directly by the envioning gas pressure and is not related to the overvoltage).
- Metal voids are not pressurized.

It is important to realise that the two cases described above represent the upper and lower limits of a spectrum of possible behaviour (a third possibility, that of an atom-ion recombination (Heyrovsky) step in quasi-equilibrium, is similar to case (ii) in that it is not conducive to high loadings); in practice, the situation will be somewhere in between such that only a *fraction* of the measured overvoltage is used to determine the chemical potential of dissolved hydrogen. This fraction is determined by the affinity distribution between the various elementary steps, which is turn is decided by the relative values of the forward and reverse reaction rates for each step. Thus, ultimately, the loading / overvoltage (or loading / current) functionality is determined by kinetic factors. Traditional electrochemical procedures may be used to induce a functionality which corresponds more closely to (the desirable) case (i) than (the undesirable) case (ii) above; for example, the addition of thiourea, which is known to increase the affinity of the Tafel step (i.e. the overvoltage at constant current under case (i) conditions), thereby preventing it reaching a state of quasi-equilibrium, and hence enhancing the loading.^{24,25}

In the event that the kinetic properties of the system are such that, in the limit, case (i) behaviour is observed (or, in the general case, that the affinity of the Volmer step is independent of overvoltage), a simple relationship may be derived for the dependence of loading on overvoltage (or current). Under case (i) conditions (referred to in the electrochemical literature as “fast discharge / slow recombination”),

$$- F \eta = \mu - \mu^* \quad (10)$$

where μ^* is the chemical potential of dissolved hydrogen with no applied overvoltage (i.e. that value corresponding to the environing hydrogen pressure). Up to loadings of about 0.8 (and perhaps beyond, although data are lacking), μ varies linearly with loading, as discussed above, and, hence

$$\eta = A x + B \quad (11)$$

where A and B are constant at a given temperature. Further, if Tafel's law is obeyed, the loading is expected to vary logarithmically with the current. Experimental verification of these relationships has been obtained,⁵ even at loadings well above those at which the linear μ , x dependence has been observed empirically.

4. Effect of temperature on loading

The results obtained above may be used to address the question: how does the loading of a palladium sample vary with temperature? In the general case, we may write:

$$\left(\frac{\partial x}{\partial T}\right)_p = \left\{ \left(\frac{\partial \mu}{\partial T}\right)_p - \left(\frac{\partial \mu}{\partial T}\right)_{x,p} \right\} / \left(\frac{\partial \mu}{\partial x}\right)_{T,p} \quad (12)$$

In the case of gas-phase loading, where equilibrium exists between the sample and the environing hydrogen, the first partial differential term on the right-hand-side of Eqn. 12 may be expressed in terms of the properties of the environing hydrogen, giving

$$\left(\frac{\partial x}{\partial T}\right)_p = \Delta S_6 / \left(\frac{\partial \mu}{\partial x}\right)_{T,p} = \Delta H_6 / T \left(\frac{\partial \mu}{\partial x}\right)_{T,p} \quad (13)$$

where ΔS_6 and ΔH_6 are the partial molar entropy and enthalpy changes, respectively, of the reaction in Eqn. 6. These are negative quantities, leading to the expected result that, in gas-phase loading, raising the temperature at constant pressure will lower the loading. Note that Eqn. 13 is a mathematical statement of Le Chatelier's principle.

In the case of electrochemical loading, where, if high loadings are to be obtained, the sample is not in equilibrium with its environment, Eqn. 13 may not be employed. Instead, we may utilize Eqn. 10 in order to cast the first partial differential term on the right-hand-side of Eqn. 12 into a more convenient form, and write

$$\left(\frac{\partial x}{\partial T}\right)_{p^0} = \left\{ -F \left(\frac{\partial \eta}{\partial T}\right)_{p^0} + \Delta S_r \right\} / \left(\frac{\partial \mu}{\partial x}\right)_{T,p^0} \quad (14)$$

where ΔS_r is the partial molar entropy change of the reaction in Eqn. 3, a negative quantity. Eqn. 14 is valid for case (i) conditions, described in Sect. 3. (Of course, case (ii) conditions correspond to Eqn. 13). In the (likely) event that an intermediate case is encountered, an additional partial differential must be added to the bracketed term in Eqn. 14 in order to include the temperature dependence of the reaction affinity for the Volmer step. Thus, in the case of electrochemical loading, a number of (ultimately) kinetically-determined factors enter into the determination of $(\partial x/\partial T)_{p^0}$, the sign and magnitude of which are difficult to predict. Under case (i) conditions, in order to ensure that the loading increases as a result of a temperature step, the overvoltage must

increase (become more negative) at constant current. The magnitude of this increase is given by Eqn. 14 if ΔS_r is known. Practically, an increasing overvoltage with increasing temperature (at first sight, an unlikely situation) might correspond to an increasingly “poisoned” recombination step (either atom-atom or atom-ion); for example, due to a change in electrode surface composition with increasing temperature. Finally, it will be noted that the value of ΔH_r is important in this context only to the extent that it contributes (partially) to ΔS_r .

5. Concluding remarks

The present discussion has centered on the properties of highly loaded compositions in the H(D)-Pd system. Unfortunately, a general absence of pertinent empirical data hampers a definitive development of many of the areas of inquiry dealt with here. In order to fully understand the properties of the highly loaded H(D)-Pd system, considerable experimental work is required in order to determine basic thermodynamic parameters for $x > 0.8$. This is particularly important if the possibility of new phase formation at elevated loadings cannot be discounted.

Acknowledgments

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List of Symbols / Nomenclature

μ = chemical potential of dissolved hydrogen	x = loading ratio, H(D)/Pd
μ^0 = a standard chemical potential	R = gas constant
D_F = Fick's law diffusion coefficient	$[H]$ = dissolved hydrogen
M = mobility	T = absolute temperature
ΔH_r = (relative) partial molar enthalpy of absorption	
$\Delta H_r(x=0)$ = as above, at infinite dilution	p = total pressure
ΔH = enthalpy change	p^0 = 1 atm. pressure
ΔU = energy change	f_{H_2} = hydrogen fugacity
V_H = partial molar volume of hydrogen	K = bulk modulus of PdH $_x$
V_{Pd} = molar volume of Pd	F = Faraday's constant
V_{H_2} = molar volume of gaseous H $_2$	

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