

Theory of hydrogen absorption in metal hydrides

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A theory of hydrogen absorption by metal hydrides is formulated in the mean-field approximation. The distinction between the true saturation and an incipient saturation is emphasized. It is shown that the incipient saturation is a manifestation of the effect of d -band structure upon the absorption of hydrogen. Absorption isotherms for Pd-H and FeTi-H systems are calculated and compared with the experimental data.

I. INTRODUCTION

The mechanism of hydrogen absorption by transition metals and alloys has been a subject of intensive investigations in recent years because of its prospective energy storage applications.¹ The amount of hydrogen absorbed by all metals, at low pressures, is proportional to the square root of the pressure of the external hydrogen gas. This is interpreted as an indication that the absorbed hydrogen is dissociated into atoms. Fowler and Smithells² classified all metals into poor absorbers and good absorbers according to the temperature dependence of the amount of hydrogen absorbed by metals. Poor absorbers can absorb only a small amount of hydrogen and the concentration of absorbed hydrogen increases only by increasing the temperature. Cu, Fe, Ni, and Pt are examples of poor absorbers. Good absorbers, on the other hand, can absorb a large quantity of hydrogen at relatively low temperatures and pressures. When the temperature is increased, the hydrogen concentration decreases. Pd, Ti, La, and Th are examples of good absorbers. The concentration of saturation absorption of hydrogen in good absorbers goes as high as 100 or 200 at. % of metallic atoms, and the metals are regarded as forming hydrides represented conveniently by chemical formulas such as PdH and TiH₂. Mott and Jones³ argued that the hydrogen atoms inside metals are ionized into electrons and protons. These protons go into some interstitial positions in the matrix of the host metal while electrons join the main body of the d -band electrons. This is most remarkably demonstrated by the paramagnetic susceptibility of Pd. Pd is a strong paramagnetic metal due to elec-

tron holes in the $4d$ band. When Pd metal is loaded with hydrogen, the paramagnetism decreases linearly with the concentration of hydrogen and this metal hydride becomes diamagnetic at and above 60 at. % of hydrogen concentration.

The high concentrations of hydrogen in many metal hydrides are interpreted as due to a cooperative condensation of absorbed hydrogen from a gaslike state to a liquidlike state. Lacher⁴ was the first to formulate a statistical-mechanics theory of hydrogen absorption by palladium. The condensation of hydrogen in metal hydrides is due to some kind of attractive interaction between hydrogen atoms. Lacher assumed this interaction to be a nearest-neighbor interaction, applied the Bragg-Williams (the mean-field) approximation, and derived absorption isotherms. Lacher's theory predicted a critical temperature below which there is a plateau (horizontal) portion of the isotherm, indicating the condensation of protons from a gaslike phase to a liquidlike phase. The theory explained qualitatively the observed features of the absorption isotherms of the Pd-H system.

One of the consequences of the mean-field approximation, as applied to hydrogen absorption, is that the critical point of absorption occurs at 50 at. % hydrogen concentration. Harasima *et al.*⁵ pointed out that the observed critical concentration of hydrogen is slightly lower than the 50 at. % value, and furthermore that there is a marked isotope effect in the shape of isotherms of heavy hydrogen by palladium. These features were theoretically explained by taking into account the effects of volume change of the metal matrix and the vibrational degrees of freedom of the absorbed protons.⁵

Still more interesting features of absorption isotherms are found in the systems such as erbium-iron hydride and iron-titanium hydride. These systems show isotherms that have two or more plateaus, i.e., the absorption takes place in several steps. Kierstead⁶ formulated a multiplateau theory for the absorption isotherms in the $\text{ErFe}_2\text{-H}$ system. The formulation is based on the postulate that there are several types of absorption sites which have different heats and entropies of absorption. The fact that there are several types of sites has been experimentally confirmed also in iron-titanium hydride¹ and even in palladium.⁷

A type of error has been made in many statistical formulations, including the original Lacher theory. This is the problem of an incorrect enumeration of the number of available sites for protons in the host metal. Since it is a rather subtle yet an important problem, let us explain it clearly by taking the palladium-hydrogen system as an example. All isotherms which have a plateau in the range of pressures shown in Fig 1 appear to approach the atomic concentration of 60 at.%, after taking off sharply upwards. It is this concentration which, in most theoretical formulations, is regarded as the saturation concentration directly representing the total number of absorption sites available for protons. For the sake of definiteness let this concentration be called the incipient saturation concentration, which should be distinguished from the true saturation concentration. Indeed, in the Lacher formulation, the number of absorption sites is assumed to be 0.6

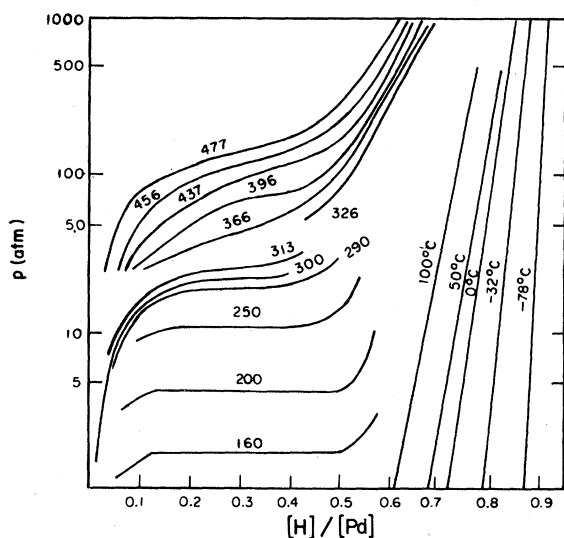


FIG 1. Pressure-concentration diagram for the Pd-H system. Experimental data (Ref. 8).

times the number of Pd atoms in the metal. If one looks at the general profile of absorption isotherms more closely, however, one notices that all of the isotherms converge to the 100-at. % concentration limit at high pressures. This 100-at. % concentration must be the true saturation concentration. It is, therefore, more reasonable to assume that the total number of hydrogen sites is equal to the number of Pd atoms, which is consistent with a crystallographic consideration. The incipient saturation can be regarded as arising from the nonavailability of electron energy levels in the d band. The energy of an extra electron increases almost discontinuously as soon as the concentration exceeds the 60-at. % value. A correct enumeration of the number of available sites for protons should be directly reflected in the calculation of the entropy, and similarly, the knowledge of the band structure is reflected in the incipient saturation. Both of those features will be fully taken into account in this formulation.

II. THEORY OF MULTIPLATEAU ISOTHERMS

For the sake of simplicity, let us work with the case of a hydride showing only two plateau isotherms. Let N_a and N_b be the numbers of available sites of type a and type b , respectively, and let E_a and E_b be their respective heats of absorption. In order to be able to deal with a cooperative absorption, we assume that protons interact with energies w_{aa} , w_{bb} , and w_{ab} , depending upon the two protons occupying the nearest-neighbor a - a , b - b , and a - b pairs of sites with coordination numbers z_{aa} , z_{bb} , and z_{ab} , respectively. z_{ab} is the number of b sites which are the nearest neighbors of an a site. Similarly, z_{ba} is defined as the number of a sites which are nearest neighbors of a b site. These numbers satisfy an obvious relation

$$N_a z_{ab} = N_b z_{ba} . \quad (2.1)$$

Let us work with the canonical-ensemble formulation in which the total number of absorbed hydrogen atoms is fixed and calculate the Helmholtz free energy for the entire lattice. Also, for simplicity, we shall work with the mean-field approximation. In this approximation, the entropy of the entire system is expressed in terms of occupation probabilities of individual absorption sites, and statistics is applied to absorption sites rather than to absorbed hydrogen atoms. Each absorption site of type a has two states, occupied and unoccupied, with probabilities η_a and $1 - \eta_a$. Similarly, the probabilities of the two states of each of absorption sites of type b are

given by η_b and $1 - \eta_b$. The total free energy of the absorbed phase is given by

$$F = F_a + F_b + N_a z_{ab} w_{ab} \eta_a \eta_b, \quad (2.2a)$$

where

$$F_a = -N_a E_a \eta_a + \frac{1}{2} N_a \eta_a \chi + \frac{1}{2} N_a z_{aa} w_{aa} \eta_a^2 + N_a kT [\eta_a \ln \eta_a + (1 - \eta_a) \ln(1 - \eta_a)] \quad (2.2b)$$

and

$$F_b = -N_b E_b \eta_b + \frac{1}{2} N_b \eta_b \chi + \frac{1}{2} N_b z_{bb} w_{bb} \eta_b^2 + N_b kT [\eta_b \ln \eta_b + (1 - \eta_b) \ln(1 - \eta_b)], \quad (2.2c)$$

and where χ is the dissociation energy of hydrogen molecule and T is the temperature. Occupation probabilities η_a and η_b satisfy the following relation:

$$\eta_a N_a + \eta_b N_b = N, \quad (2.3)$$

i.e., the total number of hydrogen atoms is fixed to be N . E_a and E_b are the heats of absorption—at infinite dilution—of type- a site and type- b site, respectively. E_a and E_b are assumed to be constants as long as the band-structure effect is ignored. The ef-

fect of the band structure will be discussed in Sec. III. Equation (2.3) indicates that only the total number of hydrogen atoms N is fixed, and protons can occupy either type- a sites or type- b sites freely.

In order to find equilibrium distributions of protons over two sublattices, the free energy is minimized with respect to the difference $\gamma = \eta_a - \eta_b$ for a given value of N . By noting the relations

$$\eta_a = N / (N_a + N_b) + (\eta_a - \eta_b) n_b, \quad (2.4)$$

$$\eta_b = N / (N_a + N_b) - (\eta_a - \eta_b) n_a,$$

where

$$n_a = N_a / (N_a + N_b), \quad n_b = N_b / (N_a + N_b), \quad (2.5)$$

$$n_a N_b = n_b N_a,$$

one finds

$$\frac{\partial \eta_a}{\partial \gamma} = n_b, \quad \frac{\partial \eta_b}{\partial \gamma} = -n_a. \quad (2.6)$$

Minimization of the free energy with respect to γ yields the condition which determines the equilibrium value of γ :

$$-E_a + E_b + (z_{aa} w_{aa} \eta_a - z_{bb} w_{bb} \eta_b + w_{ab} (z_{ab} \eta_b - z_{ba} \eta_a)) + kT \ln \frac{\eta_a (1 - \eta_b)}{\eta_b (1 - \eta_a)} = 0. \quad (2.7)$$

It is interesting to note that any one of the following three conditions would cause two plateaus to occur:

$$E_a \neq E_b, \quad z_{aa} w_{aa} \neq z_{bb} w_{bb}, \quad z_{ab} \neq z_{ba}. \quad (2.8)$$

The equilibrium condition of hydrogen inside the metal with the external gas is obtained by equating the chemical potentials of hydrogen in the two phases. The chemical potential in the metal phase is

$$\mu = \left. \frac{\partial F}{\partial N} \right|_{T, \gamma} = -n_a E_a - n_b E_b + \frac{1}{2} \chi + n_a z_{aa} w_{aa} \eta_a + n_b z_{bb} w_{bb} \eta_b + n_a z_{ab} w_{ab} \eta_b + n_b z_{ba} w_{ab} \eta_a + N n_a kT \ln \frac{\eta_a}{1 - \eta_a} + n_b kT \ln \frac{\eta_b}{1 - \eta_b}. \quad (2.9)$$

The chemical potential in the gas phase (per hydrogen atom) is

$$\mu = \frac{1}{2} [f(T) + kT \ln p], \quad (2.10)$$

where the hydrogen gas is assumed to be an ideal gas and the function $f(T)$ represents the contribution from the rotational vibrational degrees of freedom and is a slowly varying function of the temperature.

Equating the two chemical potentials, one finds the equation for the isotherms:

$$\ln p^{1/2} = -\frac{f(T)}{2kT} - \frac{n_a E_a + n_b E_b - \chi/2}{kT} + \frac{n_a z_{aa} w_{aa} \eta_a + n_b z_{bb} w_{bb} \eta_b}{kT} + \frac{(n_a z_{ab} \eta_b + n_b z_{ba} \eta_a) w_{ab}}{kT} + n_a \ln \frac{\eta_a}{1 - \eta_a} + n_b \ln \frac{\eta_b}{1 - \eta_b}. \quad (2.11)$$

As can be seen from Eq. (2.4), η_a and η_b are functions only of γ for a given value of N . The γ is found from Eq. (2.7) by means of a commonly known library subroutine for the solution of a nonlinear equation. The γ found in this way is now introduced into Eq. (2.11) and the equilibrium pressure will be found.

If one makes simplifying assumptions

$$N_a = N_b, \quad w_{aa} = w_{bb} = -w, \quad w_{ab} = 0, \quad z_{aa} = z_{bb} = z, \quad (2.12)$$

Eqs. (2.7) and (2.11) reduce to

$$-E_a + E_b - zw\gamma + kT \ln \frac{(\Theta + \frac{1}{2}\gamma)(1 - \Theta + \frac{1}{2}\gamma)}{(\Theta - \frac{1}{2}\gamma)(1 - \Theta - \frac{1}{2}\gamma)} = 0, \quad (2.13a)$$

$$\ln p^{1/2} = \frac{f(T)}{2kT} - \frac{E_a + E_b - \chi}{2kT} - \frac{zw}{kT} \Theta + \frac{1}{2} \ln \frac{(\Theta + \frac{1}{2}\gamma)(\Theta - \frac{1}{2}\gamma)}{(1 - \Theta + \frac{1}{2}\gamma)(1 - \Theta - \frac{1}{2}\gamma)}, \quad (2.13b)$$

where

$$\Theta = N/(N_a + N_b). \quad (2.13c)$$

If one makes a further simplifying assumption, $E_a = E_b = E$, one finds $\gamma = 0$, and absorption isotherm is reduced to the Lacher equation:

$$\ln p^{1/2} = \frac{f(T)}{2kT} - \frac{E - (\chi/2)}{kT} - \frac{zw}{kT} \Theta + \ln \frac{\Theta}{1 - \Theta}. \quad (2.14)$$

III. BAND-STRUCTURE EFFECT

As was mentioned in Sec. I, the incipient saturation concentration is not directly proportional to the number of available sites for protons in the host metal. The incipient saturation can result from the nonavailability of electronic energy levels in the d band. The extra electrons beyond the incipient saturation concentration must go into the higher s band as indicated by the diamagnetism of palladium containing more than 60 at. % hydrogen. Since the level density of states in the s band is much smaller than that in the d band, the energy of the extra electrons increases rapidly as the concentration of hydrogen increases beyond 60 at. %, resulting in a larger chemical potential and hence higher external pressure. This effect may be called the band-structure effect, and it must be taken into account in the formulation of hydrogen absorption. In the original Lacher theory, the incipient concentration is interpreted as the true saturation concentration, i.e.,

the total number of absorption sites is assumed to be 60 at. % of palladium atoms. From crystallographic structure considerations, it is more natural to assume that the number of absorption sites is equal to the number of metal atoms and consequently that the number of absorption sites is equal to the number of metal atoms and consequently that the calculation of the entropy should be modified. Even at the incipient saturation concentration of 60 at. % protons still have a large configurational entropy.

Indeed, from the general profile of absorption isotherms of Pd, shown in Fig. 1, all of the isotherms seem to approach the saturation concentration of 100 at. % at higher pressures, and hence it is more reasonable to assume the number of available sites for protons to be equal to the number of Pd atoms. As a demonstration of the pertinence of the band-structure effect, a simple-minded formulation will be presented as follows.⁹

One may assume that the heat of absorption E does not change appreciably until 60 at. % H on

Pd is approached, and then it changes more rapidly as the extra electrons climb up the energy-level ladder in the 5s band. This may be represented by the following dependence of the heat of absorption upon the absorption concentration:

$$E = \frac{1}{\exp[\alpha(\Theta - A)] + 1} - \Delta E \exp[\beta(\Theta - B)], \quad (3.1)$$

where Θ is the absorption concentration and α , A , ΔE , β and B are some parameters. A is the concentration below which the heat of absorption does not change appreciably, which one may choose to be 0.6. B is the concentration above which E changes more rapidly. In Fig. 2, the following values of the parameters are used in the otherwise simple Lacher equation (2.14):

$$\alpha = 20.0, \quad \Delta E = 0.10, \quad (3.2)$$

$$\beta = 10.0, \quad A = B = 0.6,$$

An overall agreement of the theoretical prediction with the experimental data is remarkable in spite of the crudeness of the underlying mean-field approximation. The preceding formulation strongly suggests that the knowledge of the combined s - d band structure is essential for the understanding of hydrogen-absorption characteristics.

IV. DOUBLE-PLATEAU ISOTHERMS ARISING FROM THE BAND-STRUCTURE EFFECT

In view of a rather remarkable consequence of the band-structure effect upon the topology of the absorption isotherms in the Pd-H system, one is encouraged to investigate a further implication of the same effect upon a double-plateau isotherm. Since the structure of the d band of transition metals is very complicated, especially when two transition metals are alloyed, as in Fe-Ti, the d band may have two or more humps. In order to demonstrate the consequences of the d -band structure having two humps, let us consider a system characterized by the same set of parameters as (3.2) except that

$$A = 0.6, \quad B = 0.9. \quad (4.1)$$

This is the case of a d band which has two humps, the first hump ending at the electron concentration of 0.6 and the second hump extending up to about 0.9, and then the energy increasing rapidly as electrons start filling the s band. The absorption isotherms for this system show two plateaus as shown

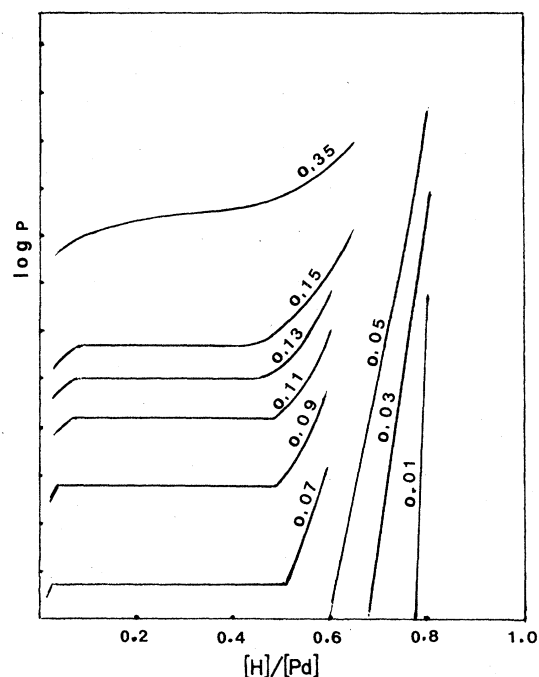


FIG 2. Pressure-concentration diagram for the Pd-H system. Theoretical curves with Eqs. (2.14), (3.1), and (3.2).

in Fig. 3, which are reminiscent of the FeTi-H system, shown in Fig. 4.¹ Since none of the experimental isotherms of the FeTi-H system has a second

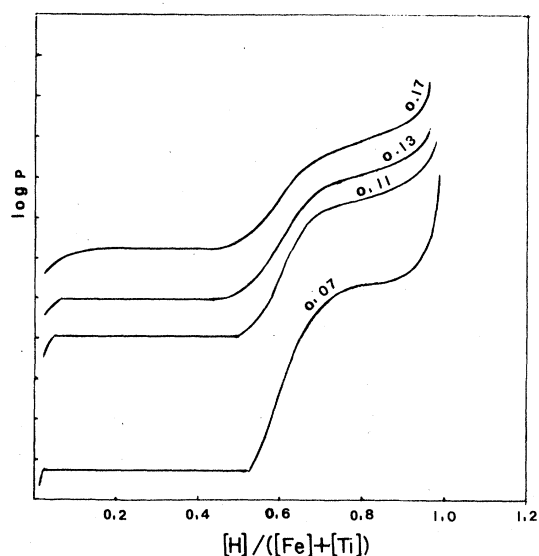


FIG 3. Pressure-concentration diagram for the FeTi-H system. Theoretical curves with Eqs. (2.14), (3.1), and (4.1).

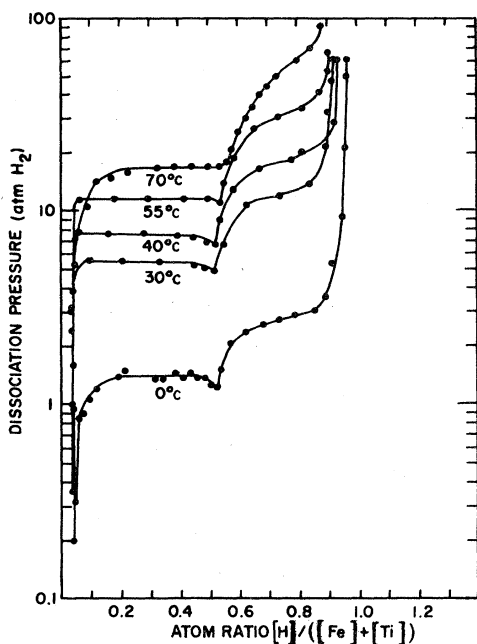


FIG 4. Pressure-concentration diagram for the FeTi-H system. Experimental data (Ref. 1).

plateau, all the temperatures of those isotherms seem to be higher than the critical temperature for the second plateau, but the topological characteris-

tics of experimental isotherms are reasonably well reproduced by the theoretical formula.

V. CONCLUSION

A mean-field-approximation theory of hydrogen-absorption isotherms in metal hydrides is presented. The theory is first applied to multiplateau isotherms, arising from the multiple sublattice structure of the proton absorption sites, and a correct statistical formulation of equilibrium isotherms is developed. It is seen that the *d*-band structure of the host metal is reflected, in a rather crucial way, in the profile of hydrogen isotherms in Pd. This is demonstrated by means of a simple model of the *d*-band structure. An overall agreement of the theoretical prediction with the experimental data for the Pd-H system is rather remarkable. A possible explanation of double-plateau isotherms of FeTi-H systems is suggested. In view of the crudeness of the underlying mean-field approximation employed in this formulation, no serious attempt is made in determining the material constants of the host metal. Delineation of the *d*-band structure of transition-metal alloys, such as Fe-Ti, by means of a careful analysis of hydrogen absorption isotherms would be an interesting subject for further investigations.

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⁹This simple-minded formulation is based on the so-called rigid-band model. Since the concentration of hydrogen in the metal hydrides is so high and hence the perturbation of hydrogen upon the electronic structure is so strong, the rigid-band model may not be valid. What is essential in this formulation is the change of the heat of absorption. There are many origins for this change, and readers are referred to the following article: A. C. Switendick, in *Hydrogen in Metals I*, Vol. 28 of *Topics in Applied Physics*, edited by G. Alfeld and J. Vökl (Springer, Berlin, 1978).