Kinetics of hydrogen absorption-desorption by niobium

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The kinetics of hydrogen absorption and desorption by clean, recrystallized Nb foils, (110) orientation, were measured as a function of temperature. The results are discussed on the basis of a previously published model for the kinetics. It was found that, contrary to the original assumption, the initial sticking coefficient of hydrogen on the clean Nb(110) surface is temperature dependent and can be described by the expression $S_i = S_0 \exp[-(2E_I/RT)]$, where S_0 was found to be close to unity and $E_I = (1.27 \pm 0.01)$ kcal/mol H. This led to a modification of the theoretical model by the inclusion of an activation energy for chemisorption. Furthermore, an analysis of the temperature-dependent data yielded values for the chemisorption energy of hydrogen $E_D = (14.8 \pm 0.2)$ kcal/mol H, the vibrational entropy at the surface, the surface coverage, as well as other parameters related to the energy barrier at the surface.

INTRODUCTION

Although much work, both experimental and theoretical, has been done on hydrogen on the surfaces of metals, until very recently few publications existed treating the problem of hydrogen on those metals which absorb hydrogen exothermically. Several authors have attempted to outline a theoretical approach to the problem of adsorption and solution[1-5] but no comprehensive theories have emerged. The problem of hydrogen absorption by metals and alloys is becoming more important as the uses of hydrogen increase. Ultimately, hydrogen will be an important secondary energy carrier. Hydrogen storage in metals has been shown to be a viable alternative to high-pressure or liquid storage. The kinetics associated with the transfer of hydrogen from the gas phase into the metal and vice versa are, therefore, of prime importance and deserve detailed study.

In a recent paper we proposed a surface-barrier model to describe the hydrogen uptake kinetics of Nb and other metals which absorb hydrogen exothermically.[6] The experiments and the related theory identified the process occurring at the surface as the rate-limiting step in hydrogen uptake by niobium. The experiments ruled out the assumption that it was the bulk diffusion process which determined the rate of uptake under the experimental condi-

tions used.

This paper indicates how the relatively easy measurement of hydrogen uptake curves can be used to determine many parameters related to the details of the solution process not readily accessible by other techniques. Figure 1 shows a diagram for the potential-energy barrier upon which the model is based. The main feature of this barrier model is the presence of a relatively deep well at the surface which ultimately governs the kinetics of the system. The strongly bound hydrogen in this well can be identified as a chemisorbed hydrogen state. Although such a barrier model has been frequently proposed in the past,[4,7] it is only recently that the resulting kinetic equations have been solved.[6] The kinetics are calculated by balancing the four fluxes at the surface indicated in Fig. 1. A detailed description of the theory is given in Refs. 6, 8, and 9. A feature of the model as presented in Ref. 6 is the assumption that the incoming flux of hydrogen is taken to be in the form of hydrogen atoms, i.e., *no* barrier for dissociation or chemisorption is included. A prediction of the model, namely, that a reduction of the chemisorption energy would enhance the rate of uptake, was shown to be fulfilled. It was demonstrated that the deposition of several monolayers of Pd or other metals on the surface of Nb and Ta could greatly enhance the uptake rate.[6,10,11] In the case of Pd the chemisorption
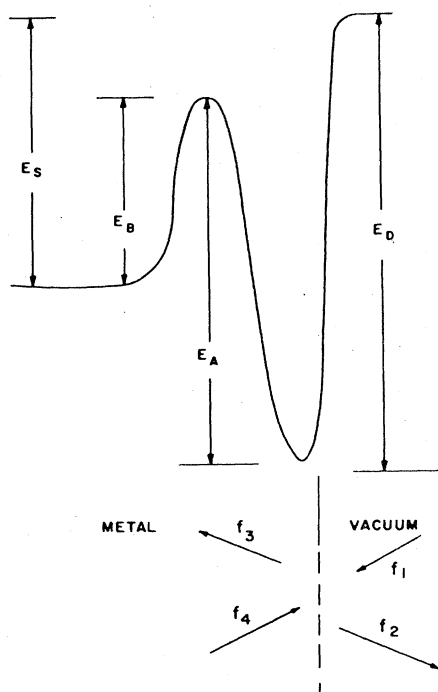
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FIG. 1. Energies defining the surface-barrier model for hydrogen absorption and/or desorption. The indicated fluxes of hydrogen to and from the surface are defined in the text.

energy for hydrogen is known to be less than that for Nb. The model was also successful in reproducing the temperature and pressure dependence of the sticking coefficient of hydrogen on Nb and resolving some of the unexplained features of previous measurements.[12]

The present paper deals with a detailed examination of the hydrogen absorption-desorption kinetics of clean niobium. It describes how the parameters of the surface barrier can be deduced from careful experiments. The experiments reveal the presence of a small activation barrier for the dissociation of hydrogen on niobium, and result in a modification of the surface-barrier model described above. Such activation barriers for dissociation have been found, e.g., on Cu(110) and (100) using molecular-beam studies.[13] However, the activation barrier found on niobium is appreciably smaller than that on copper and is therefore difficult to determine using similar techniques.

EXPERIMENTAL

The experimental procedure was similar to that described in Refs. 6 and 10. Thin foils (50 μm,

MARZ grade) of niobium, 5 mm wide by 20 mm long, were used as samples. They were supported by thick copper holders in an ultrahigh vacuum system with a base pressure in the low 10^{-10} Torr range. The samples were cleaned by resistive heating to over 2300 K in the ultrahigh vacuum after baking them in 10^{-6} Torr oxygen at 2000 K. This treatment removed most of the interstitial impurities. Analysis of the surface using Auger spectroscopy revealed no peaks other than those belonging to the substrate. After each uptake run these conditions could be reproduced by simply flashing the sample to 2300 K or higher for a short period of time. The frequent heating and cooling of the samples caused recrystallization and grain growth. Using an attached low-energy electron diffraction apparatus we observed that the grains were all aligned with their (110) planes parallel to the surface. The experimental results can therefore be taken as characteristic of the (110) plane of Nb.

The uptake rate of hydrogen was measured by monitoring the resistance as a function of time, using a four-probe technique. This technique is excellent as a measure of the hydrogen content of Nb because the rapid diffusion of hydrogen in the metal allows for a uniform distribution within the time scale of one second.[14] It is for the same reason that the diffusion of hydrogen in the bulk does not enter into the equations for the kinetics. Grain boundary effects or impurity trapping do not influence the concentration measurements at the temperatures and concentrations covered in the experiments.[15] The copper holders were used as dc current feeds. This current varied between 1 and 15 A and was used to vary the temperature of the sample. The quantity being measured was the voltage across the central part of the sample between two potential leads (0.5-mm wide, 50-μm-thick Nb foil strips spot welded to the sample about 6 mm apart). The voltage across the potential leads as well as the pressure were sampled at a rate of 10 Hz. A typical example of an as-measured uptake curve is shown in Fig. 2. The hydrogen pressure was usually 5.5×10^{-5} Torr nominally and was multiplied by a factor of 2.2 to account for the ionization probability of hydrogen compared to that of nitrogen. The voltage across the sample decreased as a function of time prior to the hydrogen inlet because the sample was cooling down after the flash cleaning which immediately preceded every measurement. This decrease prior to the hydrogen uptakes could be fitted to either an exponential or a straight line. The procedure used in the following experiments

was to wait about 100 s after the flash heating be-
fore starting the hydrogen uptake. The background
cooling could then be approximated very well by a
straight line. The next step was to subtract the
background from the experimental curve; to calcu-
late the concentration x of hydrogen in the sample
using the relationship[15]

$$\Delta\rho = 0.64 \pm 0.06 \mu\Omega\, \text{cm/at. \% H} \tag{1}$$

and to normalize the concentration by calculating
$y = x/x_{max}$, where x is the atomic fraction of hy-
drogen atoms in the bulk and x_{max} the equilibrium
value of x at the particular hydrogen pressure and
sample temperature. According to thermodynamic
measurements by Pryde and Titcomb,[16] x_{max} is
given by

$$x_{max} = \frac{P^{1/2}}{(3.954 \pm 0.338) \times 10^4}$$
$$\times \exp\left[\frac{(4.345 \pm 0.161) \times 10^3}{T}\right], \tag{2}$$

where the pressure P is measured in Torr. The
temperature T of the sample at the time of hydro-
gen uptake was determined from the resistance as-
suming a linear temperature dependence of the
resistance in this temperature range. This assump-
tion appears justified when one takes into account
measurements of the temperature dependence of
the resistivity.[17,18] The uptake part of the curve in
Fig. 2, normalized and background subtracted, is
shown in Fig. 3.

EXPERIMENTAL RESULTS AND DISCUSSION

Several parameters can be extracted from curves
such as the one shown in Fig. 3. According to our
model[6] the hydriding and dehydriding kinetics are
given by Eqs. (3) and (4), respectively:

$$\tfrac{1}{2}(1-b)^2\ln(1+y) - \tfrac{1}{2}(1+b)^2\ln(1-y) - b^2y = at\,, \tag{3}$$

$$1/y - 1/y_0 + 2b\ln(y_0/y) + b^2(y_0 - y) = at\,, \tag{4}$$

where

$$a = 2\Gamma s_0 / N_s N_l x_{max} \tag{5}$$

and

$$b = [\Theta_{max}/(1 - \Theta_{max})]\,. \tag{6}$$

Furthermore, y_0 is the value of y at the start of
dehydriding, Γ is the flux of H_2 molecules imping-
ing on the surface per cm^2 per second [see (13)], s_0
is the sticking coefficient for the bare surface, N_s is
the number of Nb atoms per cm^2 of surface, N_l is
the number of layers of Nb atoms in the sample,
and Θ_{max} is the equilibrium value of Θ, the atomic
fraction of hydrogen atoms on the surface, at the
particular hydrogen pressure and sample tempera-
ture.

By fitting the absorption curves, Fig. 3, to Eq.
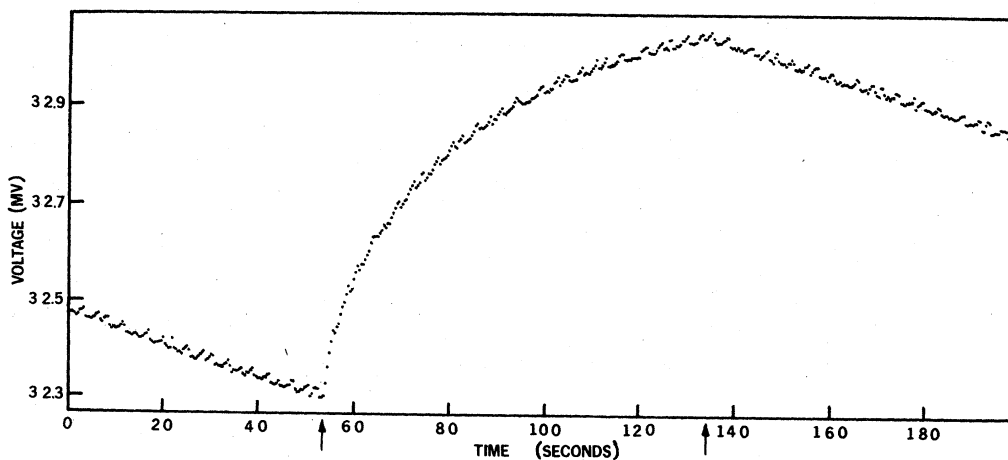(3) one can simultaneously obtain the parameters a

FIG. 2. A typical example of an as-measured uptake curve. The nominal hydrogen pressure was 5.5×10^{-5} Torr. The
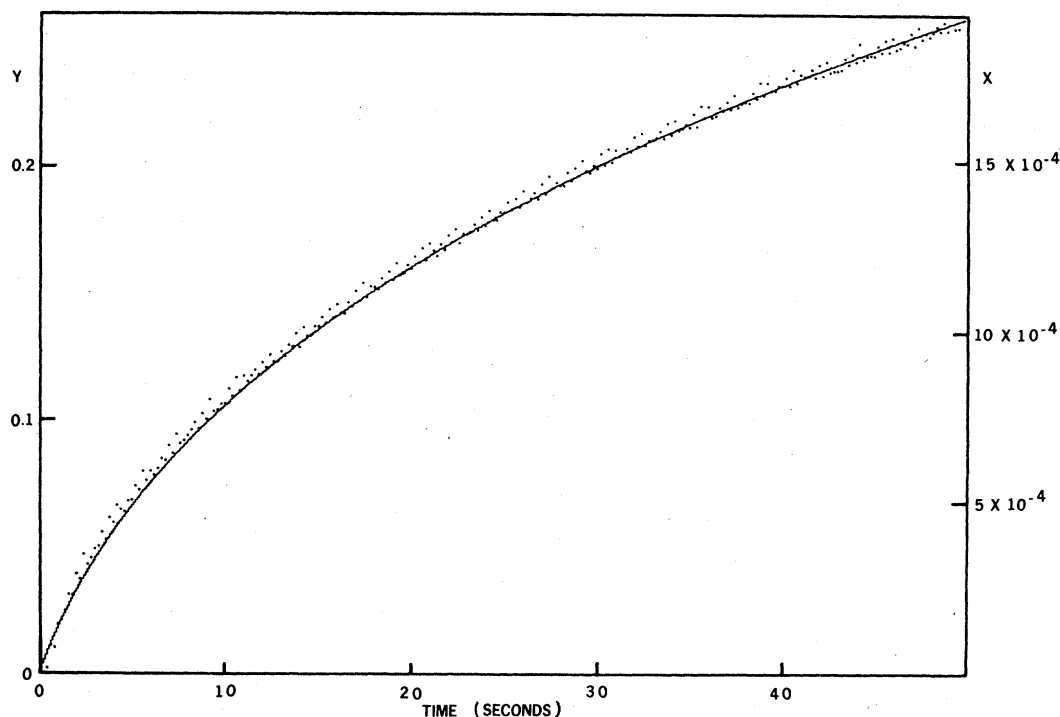current through the sample is 10 A, resulting in a sample temperature of 425.1 K.

FIG. 3. The first 50 s of the uptake curve shown in Fig. 2. The background has been subtracted and the resistivity increase translated to hydrogen concentration x and normalized to $y = x / x_{max}$. The line through the points is the theoretical curve using $a = 0.02$ and $b = 6.4$.

and b. Table I lists the a and b values obtained in this way at various temperatures. The line through the points in Fig. 3 is the calculated theoretical curve using the indicated a and b values. The fits were found to be generally excellent for the first

minute of uptake and then to deviate slightly as a function of time. This deviation is due to a deviation of the background resistivity from the assumed straight line.

The parameter a could be obtained by a second

TABLE I. The a and b parameters as well as the initial sticking coefficients derived from the absorption and desorption rates.

Temperature (K)	a From absorption	b From absorption	a From initial slope	S_i	b From desorption
503.4	0.121	0.31	0.129	0.082	
502.9	0.136	0.38	0.133	0.096	1.44
499.8	0.116	0.52	0.107	0.082	1.40
454.1	0.038	1.96	0.037	0.065	2.43
453.0	0.040	2.62	0.034	0.075	2.50
425.1	0.020	6.40	0.018	0.064	8.05
432.8	0.016	5.28	0.014	0.052	6.41
421.2	0.019	7.97	0.016	0.072	8.36
372.3	2.94×10^{-3}	44.70	2.37×10^{-3}	0.041	74.84
372.3	3.39×10^{-3}	61.50	2.37×10^{-3}	0.045	53.89
369.4	2.36×10^{-3}	48.20	1.94×10^{-3}	0.038	47.80

method, namely, from the initial slope of the normalized uptake curve:

$$\frac{dy}{dt} = a \quad \text{for } t \to 0 \ . \tag{7}$$

Evaluating a from the initial slope (for the first 3 s of uptake), one obtains values which are very close to those obtained by fitting the complete curve. These values are also listed in Table I.

One can also obtain the parameters a and b by analyzing the desorption curves, i.e., by fitting the desorption curves to Eq. (4). In this study the change in slope at the point where the hydrogen was pumped out of the systems was used to extract an independent value for b. The change in slope can be evaluated from the model. The slopes for absorption and desorption are

$$\frac{dy}{dt} = \begin{cases} \dfrac{a(1-y_0^2)}{(1+by_0)^2} & \text{for absorption} \tag{8} \\[3mm] \dfrac{-ay_0^2}{(1+by_0)^2} & \text{for desorption} . \tag{9} \end{cases}$$

The change in slope in the normalized uptake curve, when one pumps the system out after the sample has reached the normalized concentration $y_0 = x_0/x_{\max}$, is therefore

$$\Delta \frac{dy}{dt} = \frac{a}{(1+by_0)^2} \ . \tag{10}$$

This expression was used to determine the b parameters from the desorption curves using the a

parameters determined from the absorption curves. These values are also listed in Table I. These b values are in reasonable agreement with those determined from the absorption curves. However, the higher-temperature values tend to be systematically higher, indicating a possible contamination of the surface by the time desorption was initiated.

Using Eq. (3) in Ref. 6 it follows that

$$b = \left[\frac{2\Gamma s_0}{KN_s} \right]^{1/2} , \tag{11}$$

where

$$K = K_0 \exp(-2E_D/RT) \ .$$

Therefore,

$$\ln b = \frac{E_D}{R} \frac{1}{T} + \tfrac{1}{2} \ln \left[\frac{2\Gamma s_0}{K_0 N_s} \right] \ . \tag{12}$$

Plotting $\ln b$ as a function of $1/T$ will therefore yield values for E_D, the chemisorption energy, and for K_0, the preexponential factor. Such a plot is shown in Fig. 4, including all the b values; also those derived from the desorption curves. The resulting values for E_D and K_0 are $E_D = 13.5 \pm 0.2$ kcal/mol H and $K_0 = 2.75 \times 10^{14}$ s^{-1}.

THE INITIAL STICKING COEFFICIENT

Another interesting parameter which can be deduced from the data is the sticking coefficient. We define the sticking coefficient as[12]

$$s = \frac{\text{net number of H atoms entering the surface and bulk/s cm}^2}{\text{number of H atoms hitting the surface/s cm}^2} \ .$$

From the kinetic theory of gases it is known how many hydrogen molecules are hitting the surface of the sample per unit time interval and unit area at a given pressure and temperature:

$$\Gamma = \frac{3.5 \times 10^{22} P}{(2T)^{1/2}} \left[\frac{H_2 \text{ molecules}}{\text{cm}^2 \text{ s}} \right] \ . \tag{13}$$

The number of hydrogen atoms entering the sample per unit time interval can be calculated from the increase in the resistivity as a function of time. The *initial* sticking coefficients S_i, calculated from the initial slope of the resistivity, are listed in Table I for the various temperatures.

One of the assumptions of the theoretical model

is that the initial sticking coefficient is independent of the temperature. This assumption can be tested because, as stated above, the initial sticking coefficient can be measured independent of any model from the initial slope of the resistivity-versus-time curve. Figure 5 shows the result of a series of measurements designed to measure the initial sticking coefficient as a function of temperature. The data plotted shows $\ln(S_i)$ as a function of $1/T$. It is evident that the initial sticking coefficient is not temperature independent but can be written as

$$S_i = S_0 \exp[-(2E_i/RT)] \ . \tag{14}$$

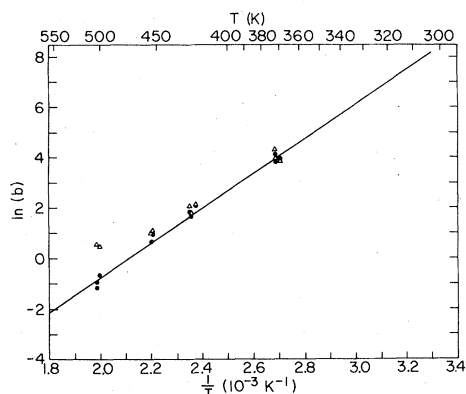From the data plotted in Fig. 5 one obtains, in

FIG. 4. The temperature dependence of the parameter b [see Eqs. (12) and (17)]. The full dots are the values derived from absorption curves; the triangles represent the values derived from the desorption curves.

kcal/mol H:

$$E_I = 1.27 \pm 0.01$$

and

$$S_0 = 0.91 \pm 0.01 \ .$$

The fact that S_0 is so close to unity shows that the initial sticking coefficient does indeed tend to that value for high temperatures. It also indicates that every site on the surface is "active," i.e., there are no so-called "active sites."

Another indication that the sticking coefficient S_0, as defined in the theory, is temperature dependent can be obtained by determining the temperature dependence of the parameter a. According to our model a is given by Eq. (5), and
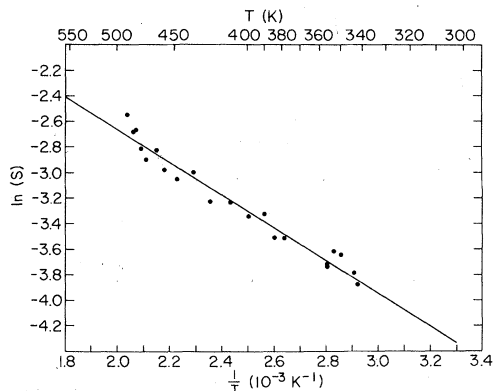
$$\ln a = \frac{E_S}{R} \frac{1}{T} + \ln \left[\frac{2\Gamma s_0}{N_s N_l C} \right] , \qquad (15)$$

where C is the pre-exponential of $x_{\max}$. Therefore, the slope of a plot of $\ln(a)$ as a function of $1/T$ should correspond to the energy of solution E_S, which is known from Ref. 16 to be (-8.633 ± 0.3) kcal/mol H. Such a plot is shown in Fig. 6 and the apparent energy of solution is found to be

$$E_S' = -(10.64 \pm 0.02) \text{ kcal/mol H} \ .$$

This can also be understood by taking into account the temperature dependence of the sticking coefficient, S_0.

In order to include this experimental observation in the theoretical description of the surface barrier, the energy diagram in Fig. 1 should be replaced by the barrier shown in Fig. 7. Calculating the kinetics based on that barrier model leads to modifications in Eqs. (15) and (12). These are then to be replaced by (16) and (17), respectively:

$$\ln(a) = \frac{E_S - 2E_I}{R} \frac{1}{T} + \ln \left[\frac{2\Gamma S_0}{N_s N_l C} \right] , \qquad (16)$$

$$\ln(b) = \frac{E_D - E_I}{R} \frac{1}{T} + \frac{1}{2} \ln \left[\frac{2\Gamma S_0}{K_0 N_s} \right] . \qquad (17)$$

Therefore,

$$E_S = -10.64 + 2E_I$$

$$= -(8.10 \pm 0.03) \text{ kcal/mol H}$$

and

$$E_D = 13.5 + E_I$$

$$= (14.8 \quad 0.2) \text{ kcal/mol H} \ .$$

FIG. 5. The temperature dependence of the initial sticking coefficient [see Eq. (14)].
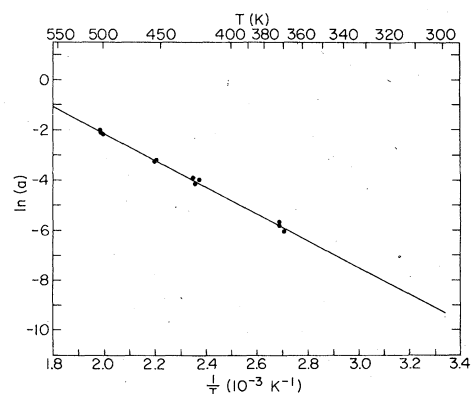

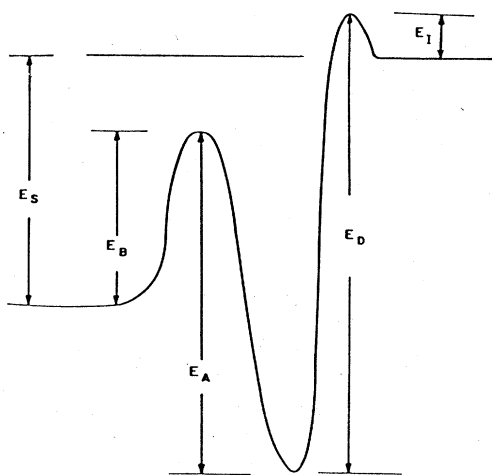FIG. 6. The temperature dependence of the parameter a [see Eqs. (15) and (16)].

FIG. 7. The surface-barrier model modified to include the activation barrier for chemisorption.

The value for the energy of solution E_S is now in reasonable agreement with that deduced from thermodynamic measurements.[16]

The barrier associated with the initial sticking coefficient can have several reasons. The most straightforward explanation would be that it is due to the difference in the potential energy, as a function of distance from the surface, of the hydrogen molecule versus the hydrogen atom. Lennard-Jones has shown how this can lead to an activation energy for chemisorption.[19] Other possibilities include that the barrier is associated with surface diffusion or defects on the surface. The fact that the S_0 is apparently 1 favors the Lennard-Jones model.

Using Eq. (6), the definition of the parameter b, the surface coverage Θ can be shown to decrease from ~ 0.98 at 370 K, i.e., almost full coverage, to ~ 0.31 at about 500 K. The presence of more empty sites at the surface leads to the more rapid uptake.

The deep well in the potential-energy diagram, which we associate with the chemisorption energy, is essentially a trap for the hydrogen at the surface. This trap can be understood in terms of the elastic strain energy required to insert a hydrogen atom into a metal. This elastic strain energy, which includes an expansion of the matrix involving primarily the shear modulus, plus the compression of the hydrogen or its associated electron density, is a positive contribution to the heat of solution. It can be considered minimized or even zero at the surface, thereby increasing the apparent heat of solu-

tion at the surface to the value of the chemisorption energy. A detailed quantitative analysis of this effect will be published elsewhere.[20] Accordingly, there should be a concentration gradient with increasing concentration towards the surface as seen by Smith[21] using electron spectroscopy.

CONCLUSIONS

It has been shown that a detailed analysis of the absorption and desorption kinetics of niobium can provide valuable information concerning the barrier to hydrogen absorption at the surface, including the chemisorption energy E_D, the solution energy E_S, the vibrational entropy at the surface K_0, the sticking coefficient S, the activation energy for chemisorption E_I, and the surface coverage Θ.

A comparison of the kinetics to those derived from our previously published model[6] shows that this model must be modified to take into account the temperature dependence of the initial sticking coefficient. This temperature dependence can be viewed as an activation barrier for the dissociation of hydrogen at the surface. This is a common phenomenon known as activated adsorption and is present in many gas-metal systems. The model as described above does imply that the hydrogen must reach thermal equilibrium with the metal surface while it is in a physisorbed molecular state.

The recent results showing that a Pd overlayer can enhance the uptake rate to such an extent that the initial sticking coefficient becomes virtually unity,[10] indicates that two features of the surface barrier must be different for a Pd(111) surface. It is this Pd surface which grows on the (110)Nb surface after the first monolayers of Pd which are commensurate with the substrate.[11]

(a) The activation energy for chemisorption E_I must be appreciably smaller than the 1.27 kcal/mol H found in this case of (110)Nb. Actually, in order to achieve unit sticking coefficient the energy E_I must be zero, i.e., nonactivated chemisorption.

(b) The chemisorption energy E_D must be less for the Pd(111) surface than for the Nb(110) surface. The latter point is known to be the case from measurements of the chemisorption energy of hydrogen on Pd(111).[4] Also, it has been deduced by some authors that chemisorption is indeed nonactivated in the case of Pd(111),[22,23] but this point requires further examination.

ACKNOWLEDGMENTS

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