

Kinetics of hydrogen absorption in transition metals and subsurface bonding

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We have modified the kinetic equations for the absorption of hydrogen in transition metals to include the effects of strong subsurface bonding. The new equations show that the subsurface, self-trapped hydrogen acts as a valve for the admission of hydrogen into the bulk. The explanation for a number of experimental facts, not well understood before, neatly follows. Discrepancies between theory and experiments found earlier are explained by the inclusion of the subsurface term into the kinetic equation.

INTRODUCTION

The absorption of hydrogen in transition metals has been a subject of recent theoretical and experimental interest. In a series of experiments¹⁻⁴ it was found that the absorption of hydrogen in the bulk is critically related to the details of the surface. In particular, it was shown that the Nb(110) surface covered with less than two monolayers of Pd absorbs hydrogen very slowly. However, when it is covered by more than three monolayers of Pd(111) the absorption into the bulk of niobium increases considerably. This is conventionally attributed to an increase in the electronic density of states at the Fermi level which enhances the dissociation of molecular hydrogen to atomic hydrogen.

The absorption kinetics (i.e., time dependence) is, however, very difficult to explain in a self-consistent manner. Pick *et al.*^{1,5} have solved a series of kinetic equations, originally written down by Conrad, Ertl, and Latta,⁶ assuming H exchange between the gas, surface, and bulk of the Nb sample. They obtain a good fit to the experimental, high-temperature, bulk uptake rates assuming a small value of the initial sticking coefficient. However, later experiments⁷ which observe directly the surface coverage, found the initial sticking S to be large. For instance, for Nb(110), $S=0.3$ compared with Pd(111) which has a sticking coefficient $S=0.1$.

Smith⁷ has measured the time dependence of hydrogen absorption by the Nb(110) surface and analyzed his data using the Pick *et al.* model. His conclusions are the following:

(i) The experimental time dependence does not follow the model at any temperature, i.e., the charging curve saturates too fast.

(ii) The time dependence of the surface coverage implies high sticking rates and slow or no equilibration between the surface and bulk.

(iii) In the temperature range $400\text{ K} < T < 600\text{ K}$ the system follows reversibly the equilibrium equations derived from Pick's model.

(iv) At room temperature the saturation value of the surface coverage coexists with a very small bulk concentration which is far from equilibrium. This implies that the surface and the bulk are decoupled at room temperature and below.

We have shown earlier⁸ that due to the interaction of the hydrogen with the surface vibrations, in certain cases, the hydrogen's binding energy increases considerably close to the surface. Quite recently, experimental evidence has also been found^{9,10} which is claimed to prove conclusively the existence of subsurface bonding, in accordance with our theoretical predictions. As a consequence, the subsurface can be saturated with tightly bound hydrogen thereby blocking the diffusion of hydrogen through the surface into the bulk. This implies that the subsurface acts as a valve, which controls the passage of H between the surface and bulk. In the present paper, we show the consequences of the strong subsurface bonding for the absorption kinetics. The existence of subsurface bonding in Nb(110) solves all the difficulties encountered by Smith in comparing the experimental data with the model of Pick *et al.* It also explains the coexistence of very high sticking coefficients and very low bulk uptake rates exhibited by clean Nb(110) surfaces in H₂ atmosphere.

In addition, generalizing the kinetics equations of Pick, we predict the existence of a critical temperature below which the surface is decoupled from the bulk and above which the surface "valve" opens thereby allowing diffusion of hydrogen through the surface into the bulk.

KINETICS

Since considerable experimental data are available for the absorption of hydrogen by the Nb(110) surface we will restrict ourselves to comparing our results with experiments in this system. However, the qualitative conclusions are of a general nature and depend only on the existence of subsurface bonding. Our earlier calculations have shown that for Nb(110) the first subsurface self-trapping energy is quite large ($\sim 0.56\text{--}0.86\text{ eV}$). This is comparable to the chemisorption energy of (0.55 eV) and, consequently, has to be taken into account. Therefore the energy of a hydrogen atom approaching the Nb(110) surface is shown schematically in Fig. 1.

This model is similar to that of Pick *et al.*^{1,2,5} except that they do not include the deep subsurface potential well. The

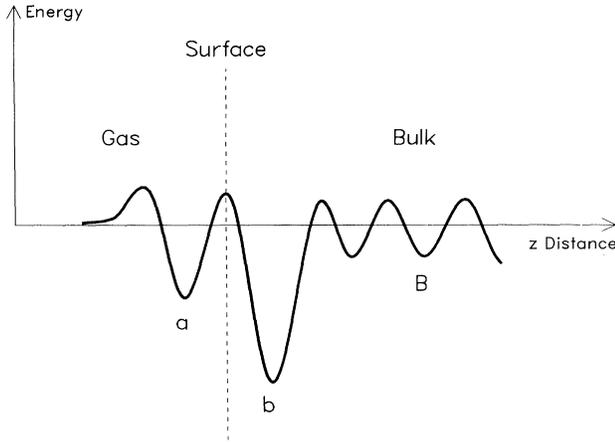


FIG. 1. Schematic energy diagram for a hydrogen atom approaching the surface of transition metal.

new kinetic equations including the subsurface bonding are

$$\frac{d\theta_a}{dt} = fs(1-\theta_a)^2 - K\theta_a^2 - k_{ab}\theta_a(1-\theta_b) + k_{ba}(1-\theta_a)\theta_b, \quad (1)$$

$$\frac{d\theta_b}{dt} = k_{ab}\theta_a(1-\theta_b) - k_{ba}\theta_b(1-\theta_a) - k_{bB}\theta_b(1-x) + k_{Bb}(1-\theta_b)x, \quad (2)$$

$$N_l \frac{dx}{dt} = k_{bB}\theta_b(1-x) - k_{Bb}(1-\theta_b)x, \quad (3)$$

where θ_a is the coverage of the chemisorption layer, θ_b is the coverage of the subsurface layer, x is the bulk concentration, f is the number of hydrogen atoms impinging on the surface per unit time and area, S is the temperature-independent sticking coefficient, K is the desorption rate, k_{ij} is the site-to-site transfer rate perpendicular to the surface and, in general, taken to be activated [$k_{ij} = k_{ij}^0 \exp(-E_{ij}/k_B T)$], and N_l is the total number of metal atoms.

In general the kinetic equations are solved numerically; however, there are several particular cases under which the equations become tractable. Following Pick *et al.*, we assume a quasistationary regime [i.e., $d\theta_a/dt = d\theta_b/dt = dx/dt = 0$, but $N_l(dx/dt) \neq 0$]. With these assumptions the equations take the form

$$J \equiv fs(1-\theta_a)^2 - K\theta_a^2, \quad (4)$$

$$J = k_{ab}\theta_a(1-\theta_b) - k_{ba}(1-\theta_a)\theta_b, \quad (5)$$

$$J = k_{bB}\theta_b(1-x) - k_{Bb}(1-\theta_b)x, \quad (6)$$

$$J = N_l \frac{dx}{dt}. \quad (7)$$

In quasiequilibrium the exchange rates between a , b , and B are much larger than the absorption rate (i.e., $J \ll k_{ij}$). Therefore, if

$$\frac{J}{k_{ij}} \ll \theta_a, \theta_b, x \ll 1 - \frac{J}{k_{ij}}, \quad (8)$$

which are the basic conditions for the existence of a quasiequilibrium regime, Eqs. (4)–(7) can be reduced to the following differential equation for x :

$$\left[1 + \left(\frac{\beta}{\nu} - 1\right)x\right]^2 \frac{dx}{dt} = f \frac{S}{N_l} (1-x)^2 - K \frac{\beta^2}{N_l \nu^2} x^2, \quad (9)$$

with $\beta \equiv k_{Bb}k_{ba}$ and $\nu \equiv k_{ab}k_{bB}$. Equation (9) is the same as obtained from Pick's model with modified β and ν .

However, it is of importance to stress that Eq. (9) is only valid if conditions (8) are obeyed. Since the subsurface binding energy is very large, the subsurface layer might saturate for even small bulk concentrations. Therefore, if $\theta_b \sim 1$, the condition (8) $\theta_b < 1 - J/k_{ij}$ might not be satisfied, and the behavior of $1 - \theta_b$ is a critical variable in the problem. At zero pressure (i.e., $f=0$) and at a temperature below the desorption temperature (i.e., $K=0$) the bulk and surface reach equilibrium, and the equation that governs the coverage is

$$(1-\theta_b) \frac{\theta_a}{1-\theta_a} = \frac{\beta}{\nu} \frac{x}{1-x} (1-\theta_b). \quad (10)$$

If $1 - \theta_b \neq 0$, Eq. (10) is a relationship between the surface coverage θ_a and the bulk concentration x . However, if the subsurface coverage $\theta_b \sim 1$, although Eq. (10) is still valid, there is no definite relationship between θ_a and x . This immediately explains one of the inconsistencies pointed out by Smith that although the hydrogen absorption was in quasiequilibrium the relationship

$$\frac{\theta_a}{1-\theta_a} = \frac{\beta}{\nu} \frac{x}{1-x} \quad (11)$$

was not obeyed at room temperature. Therefore $(1 - \theta_b)$ acts as a valve connecting the chemisorption sites to the bulk sites.

Since the value of $1 - \theta_b$ is crucial in determining when Eq. (11) is valid, we calculate its dependence on the temperature. Under the standard assumption that the transfer of particles from one level to the other is activated [$k_{ij} = k_{ij}^0 \exp[-(E_i - E_j)/k_B T]$] in quasiequilibrium Eq. (6) implies

$$1 - \theta_b = \frac{1}{(k_{Bb}^0/k_{bB}^0)[x/(1-x)] \exp(\Delta_s/k_B T) + 1}, \quad (12)$$

where $\Delta_s = E_b - E_B$ is the subsurface self-bonding energy. For Nb(110) we obtained earlier that $\Delta_s \sim 0.3-0.5$ eV $\sim 3.6-6 \times 10^3$ K.

Defining further

$$T_c(x) = \frac{\Delta_s}{k_B \ln\{(k_{Bb}^0/k_{bB}^0)[(1-x)/x]\}}, \quad (13)$$

we obtain

$$1 - \theta_b = \frac{1}{\exp\{(\Delta_s/k_B)[1/T - 1/T_c(x)]\} + 1}. \quad (14)$$

The situations of interest are the ones for which the bulk concentration x is small. Figure 2 shows the dependence of the critical temperature T_c on x , using a reasonable choice for the parameters in Eq. (13). In general, the qualitative conclusions are not critically dependent on the choice of the parameters. The transition temperature very rapidly rises above room temperature (300 K) and then the rate of increase slows down considerably. At low typical concentrations ($x \sim 0.001$), $T_c \sim 600$ K, and Fig. 3 shows the change

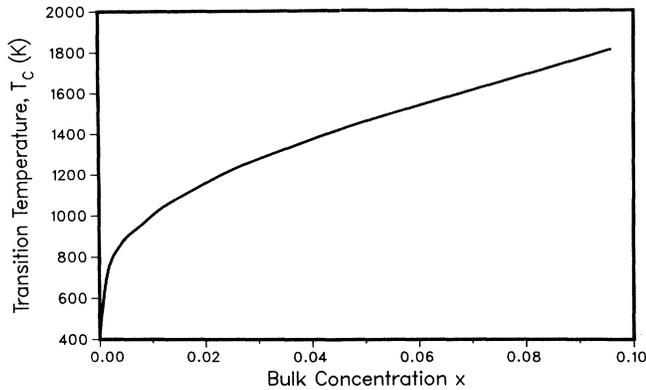


FIG. 2. Dependence of the transition temperature T_c on the bulk concentration. The parameters used in this calculation are $\Delta_s = 0.45$ eV and $k_{bB}^0/k_{Bb}^0 = 2$.

in the "surface valve" $1 - \theta_b$ as a function of temperature. This figure shows that the surface valve opens in a relatively narrow temperature range ΔT given by

$$\frac{\Delta T}{T_c} \approx \frac{kT_c}{\Delta_s} \left(\ln 10 - \frac{k_{bB}^0}{k_{Bb}^0} \frac{x}{1-x} \right) \quad (15)$$

(ΔT is the temperature range in which $1 - \theta_b$ changes from $\frac{1}{2}$ to $\frac{1}{10}$). Since the subsurface self-trapping energy Δ_s has been shown to be of the order of 0.5 eV, $\Delta T/T_c < \frac{1}{10}$ for $T_c = 600$ K.

Now it is easy to understand the full temperature dependence of the absorption observed by Smith⁷ shown in his Fig. 8. At low temperature (~ 300 K) the surface valve is closed and Pick's equations are valid with modified coefficients; however, the bulk and surface are completely decoupled. This explains the rapid surface charging of hydrogen in pure Nb to near saturation and the independence of the photoemission peak on H pressure. At higher temperatures the valve opens up slightly and therefore equilibrium is obtained between the surface and the bulk. Around 600 K the surface valve is completely open and therefore the full

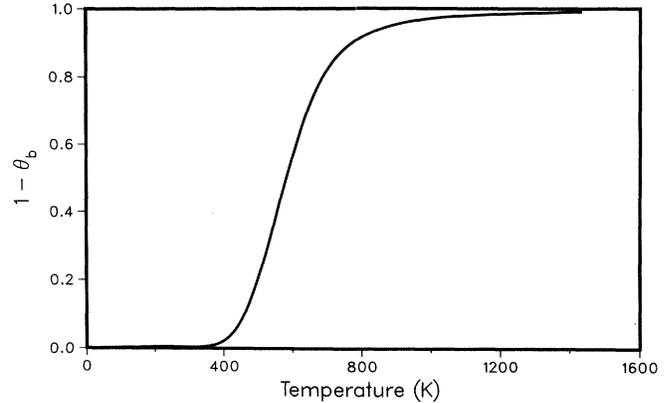


FIG. 3. Temperature dependence of the "surface valve" ($1 - \theta_b$) for $T_c = 600$ K.

kinetic equations have to be solved taking into account the strong temperature dependence of θ_b .

In conclusion, we have used a simple model which includes subsurface self-trapping to resolve the discrepancies between theory and experiment for the absorption of hydrogen in Nb. The model extends the temperature range beyond which the kinetic equation can be solved. The most important feature of this model is the existence of the subsurface valve which controls the transfer of hydrogen through the surface. This explains in a natural way the full kinetics of absorption, including the time and temperature dependence of hydrogen absorption. We hope that further experiments in an extended temperature range can critically test the ideas presented here and can be further used to determine the parameters of the theory.

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