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Surface effects on the kinetics of hydrogen absorption by metals

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We have studied a straightforward model for the kinetics of solution of hydrogen in transition metals which includes an explicit coupling between the surface and the bulk. In constrast to previous work we find that for this process there is no rate-limiting step *per se*; rather the rate equations for the two steps must be solved simultaneously. In addition, we note that for all known metals the desorption energy is larger than the solution energy (i.e., surface hydrogens are more tightly bound than bulk hydrogens). This leads to an inherent reduction in the rate of filling over the ideal rate.

I. INTRODUCTION

The problem of hydrogen in and on transition metals has attracted considerable attention recently.[1,2] However, there have been relatively few attempts to understand the interaction between the bulk and the surface. This despite the fact that hydrogen atoms adsorbed on the surface can migrate freely into the bulk and, conversely, atoms in the bulk may very well segregate to the surface. Dissolved hydrogen is one of the best known examples of a lattice gas and therefore its surface properties are of particular interest.

We wish to focus here on the kinetics of filling of the lattice when it is exposed to a uniform flux of hydrogen molecules. The simplest model for such a system in two dimensions is Langmuir's.[3] The problem is more complicated in three dimensions because the hydrogen atoms must pass through the surface to enter the bulk, so the surface can control the rate of uptake. In particular, if the heat of adsorption is larger than the heat of solution (the usual case) the surface saturates before the bulk and forms a bottleneck to further entry. Of course, the bulk concentration in equilibrium cannot be affected by the surface; only the rate of approach to equilibrium can be changed. That the surface plays a role in the kinetics of uptake has been appreciated for many years.[4–11] A review of the kinetics of uptake in Pd has been given recently by Wicke and Brodowski.[12] Wagner[4] noted that there were two extremes depending on whether or not the surface is the rate-limiting step. Our expressions reduce to his by taking the appropriate limits. However, we find for plausible parameters that there is no rate-limiting step *per se*. Rather the coupled equations for bulk and surface must be solved simultaneously. It is this feature which we believe makes our treatment unique.

Our work was motivated by recent experiments at Brookhaven Laboratory[13–19] on clean niobium and tantalum films which showed that the bulk uptake rates were orders of magnitude less than that expected without a surface bottleneck. Further, the rates could be enhanced greatly by coating the films with several layers of nickel, palladium, or platinum proving that this is a surface effect. Preliminary results have been presented elsewhere[13] and the basic model has been used to analyze other data.[15] The model has also been extended to explain photoemission data.[18,19]

In Sec. II we present the basic model and discuss the parameters which enter it. In Sec. III we present solutions valid for three different cases. Section IV covers flash desorption and Sec. V is a discussion.

II. BASIC MODEL

Since we are interested in hydrogen at low concentrations we adopt a lattice-gas model and henceforth neglect interactions between hydrogen atoms (except for the constraint that a site may be occupied by at most one H). We also assume fast bulk and surface diffusion leading to a uniform concentration in the bulk and a uniform (though different) concentration on the surface. This means we are restricting ourselves to the α phase of the metal hydride system. There is now ample evidence[20] that in the bcc metals V, Nb, and Ta the sites in the bulk are the tetrahedral sites. For the fcc metals the hydrogens occupy octahedral sites. Very little information is available on the preferred sites near the surface. In general, one would expect them to differ from the bulk and may even cause the substrate to reconstruct.[21] From vibrational data it is known that H atoms occupy the fourfold hollow[22] on Ni(100) and the threefold hollow[23] on Ni(111). It is interesting to note that these sites lie along a line which includes the octahedral site in the bulk crystal with, however, some outward relaxation. Similarly for W(100) H occupies the bridge site,[24] along a line which includes the tetrahedral site in the bulk. It has been suggested that for Ni(110) the hydrogen is slightly displaced from the equivalent octahedral site.[25]

Even if the sites are identical the energy at the sites is expected to be different in the bulk and on the surface. Following many others we expect to find an energy distribution similar to that shown in Fig. 1. Namely the surface sites are lower in energy (more negative, stronger bonds) than the bulk sites. This difference has been attributed[26] to the energy necessary to expand the metal lattice though this has been disputed.[27] Data for these energies are shown in Fig. 2 where the surface energy and bulk energy are plotted for several metals.[28,29] Note that the bulk energy varies more across the Periodic Table than the surface energy does.

Having discussed the statics we need to specify the dynamics. Since we have adopted a lattice-gas model it is natural to assume a simple jump diffusion process whereby an atom at a given site jumps to another site with frequency ν_{ij} where i and j label the initial and final site, respectively. This is the standard Chudley Elliott model[30] which has been found reasonable for H diffusion in Nb.[20] Further, Girvin and Mahan[31] have shown that the Chudley Elliott result is exact in the high T limit for a class of Hamiltonians believed to describe hydrogen diffusion. We further specialize to a one-dimensional problem and assume fast diffusion and uniform concentration in the bulk. This is reasonable at the temperatures we are considering (above 300 K). Then for the surface sites there is also the possibility of desorbing into the vacuum. We assume this to be a second-order process, the effect of which is to produce the usual Langmuir equation for the kinetics of adsorption and desorption. Namely, from the fluxes f_1 and f_2 in Fig. 1,

$$\frac{d\Theta}{dt}=\frac{2\Gamma S}{n_s}-K\Theta^2 . \qquad (1)$$

Here Θ is the atomic fraction of H atoms on the surface, Γ the flux of molecules striking the surface, S the sticking coefficient, n_s the number of substrate atoms per unit area, and K the desorption rate given by[32]

$$K \sim K_0 e^{-2E_D/kT} , \qquad (2)$$

where $K_0=10^{13}$/sec and E_D is the surface energy

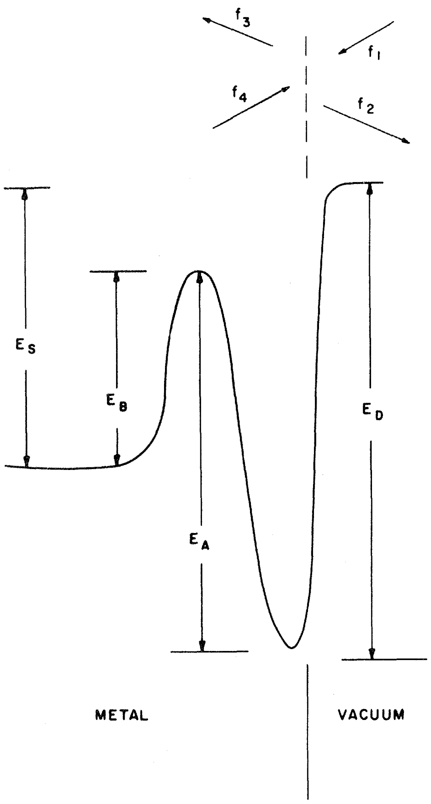

FIG. 1. Idealized potential surface for hydrogen in and on metal. The energy of the hydrogen atom at a surface site relative to H_2 in the gas phase is E_d. There is an activation barrier E_A to go into the bulk where the solution energy is E_S. f_1 is the flux at H_2 molecules incident from the gas phase, f_2 the flux of desorbing atoms, f_3 the flux from surface to bulk, and f_4 the "backflow" from bulk to surface. The four fluxes are given by

$$f_1=\frac{2\Gamma S}{n_s},\ f_2=-K\Theta^2 ,$$

$$f_3=-\nu\Theta(1-x),\ f_4=\beta(1-\Theta)x .$$

per H atom.

Following Langmuir we take the sticking coefficient to be

$$S=S_0(1-\Theta)^2\,, \tag{3}$$

although this is only approximate.[7,33] In Eq. (1), Θ should be understood as the average concentration on the outermost layer. From kinetic theory Γ is given by

$$\Gamma=\frac{P}{(2\pi mkT)^{1/2}}\,, \tag{4}$$

where P is the gas pressure and m the mass of the molecule.

We describe the coupling to the bulk by jump frequencies ν and β so that the flux from surface to bulk, f_3 in Fig. 1, is given by

$$\nu\Theta(1-x)\,, \tag{5}$$

and the return flux f_4 by

$$\beta x(1-\Theta)\,, \tag{6}$$

where x is the atomic fraction of H atoms in the bulk. We take

$$\nu=\nu_0 e^{-E_A/kT} \text{ and } \beta=\beta_0 e^{-E_B/kT} \tag{7}$$

Note from Fig. 1 that

$$-E_A+E_B+E_D=E_S\,, \tag{8}$$

where E_S is the heat of solution of hydrogen in the metal. Then the coupled equations for bulk and surface are

$$\frac{d\Theta}{dt}=2K_1(1-\Theta)^2-K\Theta^2-\nu\Theta +\beta(1-\Theta)x\,, \tag{9a}$$

$$N_l\frac{dx}{dt}=\nu\Theta-\beta(1-\Theta)x\,, \tag{9b}$$

where $K_1=\Gamma S_0/n_S$. In principle, the $\nu\Theta$ terms should be multiplied by $(1-x)$, as in Eq. (5), but we assumed here that x is small compared to 1. The more complicated treatment with $(1-x)$ included will be reported separately.[34] In Eq. (9b), N_l is the number of layers for planar geometries. This can be derived by noticing that the number of H atoms is given by xN where N is the total number of sites. From the fluxes

$$\frac{d(xN)}{dt}=An_s\nu\Theta(1-x)-An_s\beta x(1-\Theta)\,, \tag{10}$$

with A the surface area. Then more generally,

$$N_l=N/An_s\,, \tag{11}$$

the ratio of total atoms to surface atoms.

The total uptake per unit surface area is given by

$$u=N_l x+\Theta\,. \tag{12}$$

By adding the two equations in (9) we obtain

$$\frac{du}{dt}=2K_1(1-\Theta)^2-K\Theta^2\,. \tag{13}$$

In equilibrium the time derivatives vanish so that

$$\frac{\Theta}{1-\Theta}=\frac{\beta}{\nu}\frac{x}{1-x}\cong\frac{\beta}{\nu}x\,, \tag{14a}$$

and

$$\frac{\Theta}{1-\Theta}=(2K_1/K)^{1/2}\,. \tag{14b}$$

These equations give Sieverts's law which states that for small x

$$x=C_S(P/P_0)^{1/2}e^{E_s/kT}\,, \tag{15}$$

where C_S is a constant given experimentally[5] as 2.30×10^{-7} when $P_0=10^{-5}$ Torr.

All of these parameters are further restricted in equilibrium by statistical considerations. In particular the chemical potential of the two-dimentional lattice gas is

$$\mu_s=-E_D+kT\ln\left[\frac{\Theta}{1-\Theta}\right]. \tag{16}$$

For an ideal gas, neglecting vibration and rotation

$$\mu_g=kT\ln\left[n\left[\frac{2\pi\hbar^2}{mkT}\right]^{3/2}\right], \tag{17}$$

where n is the gas-phase particle density.

The condition for equilibrium is

$$\mu_s=\tfrac{1}{2}\mu_g\,, \tag{18}$$

or

$$\frac{\Theta}{1-\Theta}=e^{E_D/kT}n^{1/2}\left[\frac{2\pi\hbar^2}{mkT}\right]^{3/4}. \tag{19}$$

Compared with Eq. (14) we find

$$\frac{K_0 n_S}{S_0}=2\pi\frac{mk^2T^2}{\hbar^3}\,. \tag{20}$$

More generally, the vibrational states can be included by multiplying the factor $\Theta/(1-\Theta)$ in Eq. (16) by Z_v the vibrational partition function. We expect, however, that the vibrational modes have energies in the 100-meV range which is large compared with kT so $Z_v \simeq g$, the degeneracy of the mode. The effect of rotational modes in the gas phase may be important in practice but we neglect it here.

Similar considerations apply to the equilibrium between the bulk and the gas. The result is

$$\frac{x}{1-x} = e^{E_S/kT} n^{1/2} \left[\frac{2\pi\hbar^2}{mkT} \right]^{3/4} , \tag{21}$$

which (neglecting x compared with 1) yields Sieverts's law, without any kinetic arguments.

III. LIMITING FORMS

General solutions of the coupled nonlinear equations [Eq. (9)] have not been found. Computer calculations were obtained for a wide range of parameters and valid analytical approximations found for various time intervals. Before these are discussed, let us consider several limiting cases. Two of these have been treated previously by Wagner.[4] The first corresponds to very small surface barrier so that we may take $\Theta = x$. Namely, the bulk and surface concentrations are equal at all times. From Eq. (13) then

$$(N_l+1)\frac{dx}{dt} = 2K_1(1-x)^2 - Kx^2 , \tag{22}$$

which immediately integrates to

$$\frac{x}{1-x} = \left[\frac{2K_1}{K} \right]^{1/2} \tanh \left[\frac{(2K_1K)^{1/2}}{N_l+1} \right] . \tag{23}$$

These solutions exhibit an initial uptake rate which varies linearly with pressure and is nearly independent of the temperature. For degassing one has, by setting $K_1 = 0$,

$$\frac{x}{1-x} = z = \frac{z_0}{1+z_0Kt} , \tag{24}$$

where

$$z_0 = \left. \frac{x}{1-x} \right|_{t=0} . \tag{25}$$

These results may be characterized as "ideal filling" since no faster uptake rate can be obtained.

The second case corresponds to very large surface barrier, so that the surface and gas come into equilibrium before there has been appreciable flow into the bulk. In this case we solve Eq. (9a) with $v=0$ and $x=0$. This is the usual Langmuir equation. Then, we can insert the equilibrium value of Θ into Eq. (9b) to find the uptake rate. The solution is given in Eq. (46) where we discuss it further. Here, we simply note that the initial uptake rate varies like the square root of the pressure and exponentially with temperature.

These two limits also correspond to the condition that the rate-limiting step is arrival from the gas phase for the first case and surface to bulk transfer in the second case. In our numerical studies described in detail in Sec. IV we found another simple limit which seems to describe well the uptake rates for niobium films and films coated with palladium. In this limit the bulk and surface come into equilibrium long before the gas has come into equilibrium with the sample (bulk plus surface). This occurs because the jump rate from surface to bulk and the "back flow" from bulk to surface are both orders of magnitude larger than the arrival rate from the gas. This condition could not occur for an infinite bulk because the backflow would be negligible. On the other hand, an infinite bulk would never fill up either. The backflow must also be zero at $t=0$ so this equilibrium can only exist past an initial transient. The equilibrium between bulk and surface means that the surface concentration and bulk concentration are related by a Boltzman factor. Now, the solution energy is always less in magnitude than the desorption energy (see Fig. 2) and so the surface concentration Θ is always larger than the bulk concentration x. In other words the surface saturates before the bulk and slows the whole process. Note that this is not the same as saying that there is a large

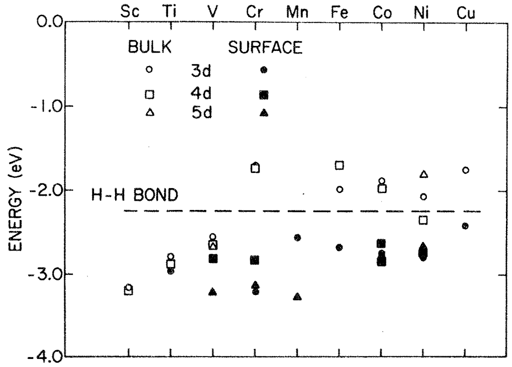

FIG. 2. Bond energy of hydrogen for chemisorption (surface) and solution (bulk). Data from Refs. 28 and 29. The bond energy for the bulk is given by the heat of solution per H atom, plus one-half the dissociation energy of H_2.

barrier between surface and bulk. There is in fact rapid transfer across this barrier. But there is equally rapid return. The slowing down is due to the factor $(1-\Theta)^2$ in Eq. (9a). For Θ near 1 surface hydrogens are blocking incoming hydrogens. In general, the exact form for this factor may differ from $(1-\Theta)^2$ but it should still be true that the blocking effect occurs for $\Theta\rightarrow 1$. We found that by inserting the equilibrium relation Eq. (14a) in the rate equations we were able to integrate the differential equation. This is described in Sec. IV in Eqs. (34) and (35).

IV. NUMERICAL RESULTS

For a discussion of the computer results and the corresponding analytical approximations it is convenient to define the following quantities

$$b=\left[\frac{2K_1}{K}\right]^{1/2}, \tag{26}$$

and the maxima in x and Θ

$$\begin{aligned} x_m&=\frac{\nu b}{\beta}, \\ \frac{\Theta_m}{1-\Theta_m}&=b . \end{aligned} \tag{27}$$

Note that b is a function of pressure and temperature while β/ν depends only on temperature.

The computer results for dx/dt and $d\Theta/dt$ as a function of $\ln t$ are sketched in Fig. 3. These were obtained with parameters applicable to hydrogen on Nb or Ta as well as thin Pd and Pt layers on Nb, namely

$$\begin{aligned} \nu &>> 2K_1 , \\ \nu &>> K\Theta . \end{aligned} \tag{28}$$

These conditions are expected to be applicable to most hydrogen-metal systems. Under these conditions the following analytical approximations were found to be in excellent agreement with the computer results over the time intervals indicated:

$$\left.\begin{aligned} N_l\frac{dx}{dt}&=2K_1(1-e^{-\nu t}) \\ \frac{d\Theta}{dt}&=2K_1e^{-\nu t} \end{aligned}\right\} \quad 0<t<t_1 , \tag{29}$$

$$\left.\begin{aligned} N_l\frac{dx}{dt}&=2K_1 \\ \frac{d\Theta}{dt}&=\frac{2\beta K_1}{\nu N_l} \end{aligned}\right\} \quad t_1<t<t_2 , \tag{30}$$

$$\left.\begin{aligned} N_l\frac{dx}{dt}&=\frac{2K_1-K(\beta^2/\nu^2)x^2}{(1+(\beta/\nu)x)^2} \\ \frac{1}{(1-\Theta)^2}\frac{d\Theta}{dt}&=\frac{\beta}{\nu}\frac{dx}{dt} \end{aligned}\right\} \quad t>t_1 , \tag{31}$$

with t_1 and t_2 given by

$$\begin{aligned} t_1&=\frac{1}{\nu}\ln\frac{\nu N_l}{\beta}, \\ t_2&=0.01\frac{\nu N_l}{2K_1\beta}, \quad b>0.1 \\ t_2&=0.1\frac{\nu N_l b}{2K_1\beta}, \quad b<0.1 . \end{aligned} \tag{32}$$

These results are also indicated in Fig. 3.

Equation (29) represents the earliest transient and comes from the approximation

$$\frac{d\Theta}{dt}=2K_1-\nu\Theta .$$

The plateau region is given by Eq. (30). Equation (31) is valid from t_1 since it reduced to Eq. (30) for small x and Θ. Equation (31), which is equivalent to a quasiequilibrium approximation, is proven valid after a short transient and is discussed in detail below. In general, the following comments may be made:

(i) t_1 is independent of the pressure but is a

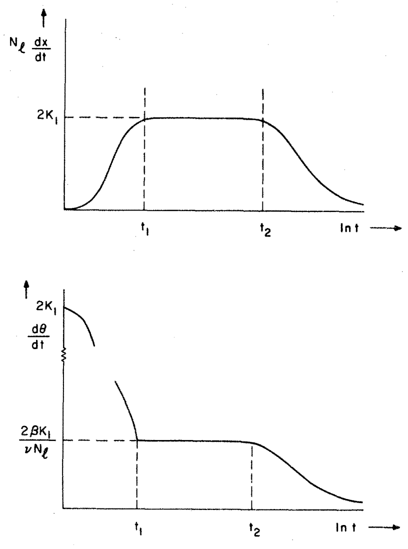

FIG. 3. Schematic behavior of rates versus ln (time).

strong function of the temperature and increases rapidly with decreasing temperature. Thus, if one wants to study the transient, experiments at low temperature are needed.

(ii) At a given temperature, t_2 varies as the reciprocal of the pressure, i.e., an increase of a factor of 10 in the pressure decreases t_2 by a factor of 10 (except at extremely low pressures).

(iii) At a sufficiently high pressure and/or low temperature the condition $t_1 < t_2$ is violated and the plateau region of dx/dt of Fig. 3 coalesces into a maximum (at high pressure t_2 becomes small, at low temperature t_1 becomes large).

All these statements are, of course, in agreement with the computer solutions.

The most pertinent approximation is that of Eq. (31). As discussed in Sec. III and previously,[13] this approximation describes accurately the H uptake by Nb films. An equivalent way of stating this approximation is that x and Θ are in quasiequilibrium, i.e.,

$$x = \frac{\nu}{\beta}\frac{\Theta}{1-\Theta} , \tag{33}$$

even though x and Θ separately have not attained their equilibrium values. With this approximation and with $d\Theta/dt$ very samll compared to $N_l(dx/dt)$ the integration can be performed to yield, for charging

$$\tfrac{1}{2}(1-b)^2\ln(1+y) - \tfrac{1}{2}(1+b)^2\ln(1-y) - b^2 y = at , \tag{34}$$

where $y = x/x_m$ and $a = 2K_1/(N_l x_m)$. For degassing, by setting $K_1 = 0$ in Eq. (31) one obtains

$$1/y - 1 + 2\frac{\beta}{\nu}x_0\ln(y) + \frac{\beta^2}{\nu^2}x_0^2(1-y) = \frac{1}{N_l}K\frac{\beta^2}{\nu^2}x_0 t , \tag{35}$$

where y is now x/x_0 and x_0 is the concentration at $t=0$. The initial slopes are $dy/dt = a$ for charging and

$$\frac{dx}{dt} = -\frac{1}{N_l}K\left[\frac{\beta}{\nu}\right]^2 x_0^2 \bigg/ \left[1+\left[\frac{\beta}{\nu}\right]x_0\right]^2$$

for degassing.

As an illustration of the behavior of Eqs. (34) and (35) we have plotted the normalized concentration y for charging and degassing as a function of time for various values of the desorption energy (see Fig. 4). The constant a in Eq. (34) was chosen to be 0.1 per sec and b was varied from 0 to 100. Hence the temperature and pressure is the same for all curves. This in turn means that the equilibrium concentration in the bulk is the same for all cases and x is normalized to that value so the $y \rightarrow 1$ as $t \rightarrow \infty$. Varying the desorption energy now amounts to varying b in Eq. (34). From Eq. (27) we see that large values of b imply $\Theta_m \rightarrow 1$ and small values to $\Theta_m \rightarrow 0$. Hence, small b implies a more open surface and rapid approach to equilibrium while large b implies that the surface saturates long before the bulk and the approach to equilibrium is retarded. We believe that this feature explains the dramatic change in rate of uptake of Nb when thin Pd overlayers are added because desorption energy for Pd is less than that for Nb.

We also note that Eq. (34) reduces to the ideal filling case discussed previously when $b \rightarrow 0$. Then Eq. (34) reduces to

$$\tfrac{1}{2}\ln\left[\frac{1+y}{1-y}\right] = at$$

and the left-hand side of this expression is equivalent to $\tanh^{-1}y$.

In a similar way the degassing curves illustrate the effect of varying the desorption energy at fixed temperature. In this case $y = x/x_0$ with x_0 the concentration at $t=0$. The constant $x_0 K(\beta/\nu)^2 N_l$ on the right-hand side of Eq. (35) has been set to 0.1 per sec and the constant $(\beta/\nu)x_0$ was varied from 0 to 8. Again, small values of the desorption energy imply that $(\beta/\nu)x_0$ is small and leads to rapid degassing.

Several extensions of the basic model were also investigated. If a physisorbed precursor is included in the model one can write three nonlinear differential equations analogous to Eq. (9). Similar

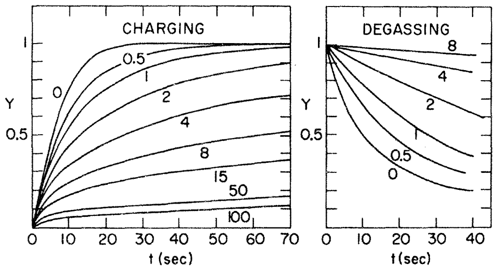

FIG. 4. Normalized concentration y versus time calculated from Eqs. (34) and (35) for different values of the desorption energy at constant T and P as discussed in the text.

analytical approximations can be made but with two quasiequilibria the algebra becomes cumbersome. The main conclusion we arrived at was that the kinetics is not altered in a drastic way by the physisorbed precursor although the time scale may be changed. Basically the approach to equilibrium is slowed down, as might be expected.

A more important consideration has to do with the thickness of the barrier region which in the basic model was assumed to be essentialy zero. This point is of importance for composites, e.g., a layer of Pd on Nb.

As the thin layer of the composite, the barrier layer, is increased in thickness one has to take the transit time across the layer into account as well as the fact that there are now two interfaces (gas layer and bulk layer). The model becomes considerably more complex but can be treated by models and methods analogous to the basic model. There is, of course, a general slowing down of the process due to the additional layer transit time, but the overall response is still like that of Fig. 3. Computer calculations and some analytical approximations indicated the following. The time of the transient increased roughly linearly with the number of barrier layer planes n_b, i.e., on the diagram of Fig. 3 t_1 became larger. t_2 increased much more slowly and, therefore, the plateau interval t_2-t_1 decreased with increasing n_b. As n_b was increased further the plateau collapsed into a maximum with a concomitant decrease in the value of the maximum. Qualitatively the variation in t_1 is similar to a decrease of temperature.

V. FLASH DESORPTION

For adsorbates it is usually found that the surface energy can be estimated from a flash-desorption experiment. This means that the temperature is increased linearly with time. Assuming a constant pumping speed the pressure measured in the vacuum chamber will first rise and then fall as the surface is depleted. From the kinetics, a maximum in the desorption rate will occur for some temperature which can be roughly correlated with the surface energy. The purpose of this section is to point out that these estimates can be greatly altered when hydrogen can diffuse into the bulk.

The linear heating experiment is started with a given concentration x_0 in the bulk (i.e., the system was charged at some temperature and then quenched to a lower temperature where the desorption rate was insignificant). As the temperature is raised the parameter b of Eq. (31) becomes small and the degassing rate, with the quasiequilibrium approximation, may be written

$$\frac{dx}{dt}=-\frac{K_0'}{N_l}e^{-T_0/T}x^2 , \tag{36}$$

where

$$K_0'=\frac{K_0\beta_0^2}{\nu_0^2}$$

and

$$T_0=\frac{1}{K}(2E_D+2E_B-2E_A)=2E_s/k .$$

Since rates are negligible at low temperature one can write

$$T=\alpha t ,$$

and Eq. (36) becomes

$$\frac{dx}{dT}=-\frac{K_0'}{\alpha N_l}e^{-T_0/T}x^2 . \tag{37}$$

Following Dienes and Vineyard[35] the solution of this equation is given by

$$\int_{x_0}^{x}\frac{dx}{x^2}=\frac{-K_0'}{N_l}\frac{T_0}{\alpha}\left[\frac{T}{T_0}e^{-T_0/T}+\mathrm{Ei}\left[\frac{-T_0}{T}\right]\right] , \tag{38}$$

where $\mathrm{Ei}(-x)$ is the exponential integral, which can be approximated by

$$\mathrm{Ei}(-x)\cong e^{-x}\left[\frac{1}{x^2}-\frac{1}{x}\right]$$

for $x>>1$, i.e., $T/T_0<<1$, which is satisfied during the greater part of the desorption. With this approximation and upon taking the integral on the left-hand side of Eq. (38), one obtains

$$\frac{1}{x}-\frac{1}{x_0}=\frac{K_0'}{N_l}\frac{T_0}{\alpha}\left[\frac{T}{T_0}\right]^2 e^{-T_0/T} . \tag{39}$$

The maximum in dx/dT occurs at T^* and x^* given by the condition

$$\frac{d^2x}{dT^2}=0=-2\frac{dx}{dT}\bigg|_{\max}-x^*\frac{T_0}{(T^*)^2} . \tag{40}$$

Upon substitution from Eq. (37)

$$\begin{aligned}\frac{1}{x^*}&=\frac{2K_0'}{\alpha N_l}\frac{(T^*)^2}{T_0}e^{-T_0/T^*}\\&=\frac{1}{x_0}\frac{K_0'}{\alpha N_l}\frac{(T^*)^2}{T_0}e^{-T_0/T^*} ,\end{aligned} \tag{41}$$

and, therefore,

$$x_0 \frac{K_0' T_0}{N_l \alpha} \left[\frac{T^*}{T_0} \right]^2 e^{-T_0/T^*} = 1 \; , \tag{42}$$

which gives the relation between α and T^* and can be used directly to evaluate T_0 if measurements are made for several heating rates[36] (T^* increases with increasing α). Furthermore, from Eqs. (41) and (39),

$$\frac{x_0}{x^*} = 2 \; ,$$

and, therefore, from Eq. (40),

$$-\frac{1}{x_0} \frac{dx}{dT} \bigg|_{\max} = \frac{T_0}{4(T^*)^2} \; , \tag{43}$$

which is a function of T^* only, but T^* of course is a function of α according to Eq. (42). $dx/dT\,|_{\max}$ decreases with increasing α.

An equivalent treatment applies to desorption from a surface (no interaction with the bulk) with the following changes in Eq. (42):

$$x_0 \rightarrow \Theta_0 \sim 1, \; N_l \rightarrow 1, \; T_0 \rightarrow T_0' = 2E_D/kT,$$

$$\beta_0/\nu_0 \rightarrow 1 \; .$$

Under these conditions a crude estimate of E_D can be made since it depends only logarithmically on the other parameters of Eq. (42). As a useful rule of thumb the value

$$\frac{T_0'}{T^*} \sim 30 \tag{44}$$

has often been used.

The point we wish to make here is that a similar crude argument can be made for the bulk but with a significantly large quantitative change. This is because the x_0/N_l factor can easily be about 10^{-8} so far the same set of parameters

$$\frac{T_0}{T^*} \sim 11 \; . \tag{45}$$

VI. DISCUSSION

While lattice-gas models and jump diffusion have been used to understand hydrogen-metal systems for many years there have been relatively few attempts to treat bulk and surface properties on the same footing. We believe our model is the simplest one possible in that we assume fast diffusion and neglect interactions between hydrogen atoms.

As already indicated, this model has been successful[13–17] in describing and interpreting recent experiments on hydrogen absorption by pure Nb and Ta as well as by thin overlayers of Pd and Pt. Charging rates as well as degassing rates as functions of pressure, temperature, and thickness of overlayer were described quantitatively with reasonable values of the various energies involved.

We discuss briefly several related models that have been presented previously. Wagner[4] noted many years ago that there were two limiting cases. The first corresponds to assuming that the rate-limiting step is surface to bulk transfer. Then the surface and gas come into equilibrium and from Eq. (9) we obtain

$$N_l \frac{dx}{dt} = \frac{\beta}{1+(\beta/\nu)x_m}(x_m - x) \; , \tag{46}$$

where x_m is the equilibrium concentration. Wagner's second limit corresponds to our ideal filling case treated previously [Eq. (22)].

Pryde and co-workers[5] have studied the isothermal rate of evolution of H from Ta and Nb assuming bulk-surface equilibrium and surface control of the desorption rate. This is the long-time limit of our model. Namely, we take x sufficiently small so that $bx << 1$ in Eq. (31), then [as in Eq. (36)]

$$\frac{dx}{dt} = -cx^2 \tag{47}$$

or

$$\frac{1}{x} - \frac{1}{x_0} = ct \; . \tag{48}$$

The conditions of their experiment were such that the pressure in the cell was given by

$$P = -\gamma \frac{dx}{dt}$$

with γ characteristic of the vacuum system. Then,

$$(\gamma/P)^{1/2} - (\gamma/P_0)^{1/2} = c^{1/2} t \; , \tag{49}$$

and

$$c^{1/2} = K^{1/2} \frac{\beta}{\nu} \frac{1}{N_l^{1/2}} \propto e^{-E_s/kT} \; , \tag{50}$$

from which one can determine the solution energy directly.

Another rate expression similar to ours was found empirically by Auer and Grabke.[9] They measured the hydrogen desorption rate from Pd films (which were not in ultrahigh vacuum). They suggested a physically more complex model involving two surface states characterized by two different adsorption energies. They assume that both states are in equilibrium with the bulk but one has a concentration which is small compared with 1. They then obtain, for desorption,

$$\frac{dx}{dt}=-\frac{KBB'x^2}{1+Bx}\ , \tag{51}$$

the form of which differs from ours only in the denominator. It would be interesting to compare these two rate expressions with data taken on clean metal surfaces.

Recently, Feibelman, Hamann, and Himpsel[37] have compared photoemission experiments with detailed calculations for hydrogen on titanium (0001). They have found that overlayer sites are generally more tightly bound than underlayer sites by 0.5 – 1 eV which is roughly consistent with Fig. 2. Also Eberhardt, Greuter, and Plummer[38] have investigated the adsorption of H on Ni, Pd, and Pt(111) surfaces at low temperatures. They find that the H's adsorb into surface sites but upon warming they irreversibly move into subsurface sites. Both of these papers point out again the importance of considering the surface bulk interface and not interpreting all experiments as due only to surface or only to bulk effects.

Finally, our model has been used to interpret the unusual behavior observed in flash desorption experiments of H_2 on Nb by Ko and Schmidt.[8] As shown by Pick and Greene,[15] the sticking coefficients are well described as functions of temperature, pressure, and coverage with a very reasonable value of the chemisorption energy.

Regarding the enhancement of the uptake rates with Pd overlayers this comes about naturally in our model[13] because the desorption energy on Pd is less than Nb by about 0.1 eV (1.6 kcal/mol H) so that for the composite system, surface and bulk energies are more nearly equal and the surface does not saturate before the bulk. Of course, other factors could limit the uptake rate in other circumstances such as oxygen contamination, diffusion through the overlayer, or inability of the overlayer to dissociate hydrogen. But in any event we believe the surface saturation discussed in this paper plays an important role.

In conclusion, we have constructed a simple model for hydrogen absorption by metals which has the following features. It reduces to Langmuir's model in the case where there is adsorption but no absorption. It reduces to Wagner's two limits when the chemisorption energy is (a) much larger than the solution energy or (b) equal to the solution energy. In realistic cases (Nb or Pd) it predicts that neither of Wagner's limits is appropriate but rather the bulk and surface must be treated on an equal footing.

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