

Reply to "Comments on the kinetics of hydrogen uptake on niobium surfaces"

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We show that the conclusions presented in the preceding Comment regarding the kinetics of hydrogen absorption by niobium are incorrect. We present a critical comparison of theory and photoemission data as well as possible experimental tests.

The preceding Comment¹ makes a comparison between experimental data and a numerical calculation based on our earlier work,² using a specific set of parameters. Based on this comparison, the authors claim our calculations lack validity to the kinetics of hydrogen absorption by the niobium (110) surface at room temperature. We show that the comparison of experiment and calculation presented by these authors is incorrect because (a) in certain limits the numerical results are incorrect, (b) a direct comparison of the kinetics of hydrogen absorption and the kinetic equations is not possible unless the parameters are independently determined, and (c) the relationship between experiment and theory is only possible if further understanding emerges regarding the meaning of photoemission data. Here, we will address principally point (c) since this is the crucial point as far as comparison of theory and experiment is concerned. There are, however, specific experimental tests which can be performed to further test our theoretical ideas.

We have earlier shown that in certain particular cases [for instance Nb(110)] the energy of a hydrogen atom is lowered considerably due to the interaction with the surface phonons.^{3,4} This has as a consequence that at low temperatures the hydrogen is trapped close to the surface ("subsurface bonding"). This has been experimentally confirmed in a variety of experiments⁵⁻⁸ including possibly those by the authors of the previous Comment.¹ Later we modified the kinetic equations earlier advanced by Pick,⁹ to include the effect of subsurface bonding on the kinetics of absorption of hydrogen. As a consequence of the continuity conditions, the kinetics is governed by three coupled differential equations with seven parameters.² As a consequence, it is obvious that at low temperature if the subsurface site (site *b* in the notation of Ref. 2) is blocked, i.e., $\theta_b = 1$, the surface is decoupled from the bulk. This is so because, it is highly improbable to transfer hydrogen atoms directly from the gas to the second or third subsurface site. This was cast in the mathematical formalism through a discussion of Eq. (10) in Ref. 2.

Dienes, Strongin, and Welch¹ present a disagreement between experimental data of Strongin, Colbert, Dienes, and Welch¹⁰ and a numerical calculation using our formalism with several of the parameters unspecified. This disagreement can be expected from the very beginning since the authors interpret erroneously the experimental results. A discussion of the details of the computer calculations and the parameters is of minor relevance and that is why we will

mainly address ourselves to the interpretation of the experiments.

Figure 1 reproduces the data and calculation presented by the previous Comment as a function of the relevant variable, the exposure. In addition, we present Smith's¹¹ data on photoemission intensity of a Nb surface exposed to H₂ for two different photon energies. Smith's data clearly show that the photoemission intensity is very strongly photon energy ($h\nu$) dependent. The photoelectron spectrum (split off the Nb *d* band) characteristic of the surface (or subsurface) hydrogen grows very fast for $h\nu = 21.2$ eV; however, a much slower growth is obtained for $h\nu = 11.8$ eV. For $h\nu = 21.2$ eV the saturation seems to be exponential, whereas $h\nu = 11.8$ eV suggests second-order sticking. The order of the sticking cannot be photon energy dependent and therefore further understanding of the meaning of the photoemission data is necessary before a detailed comparison with parameter-dependent, numerical calculations is performed.

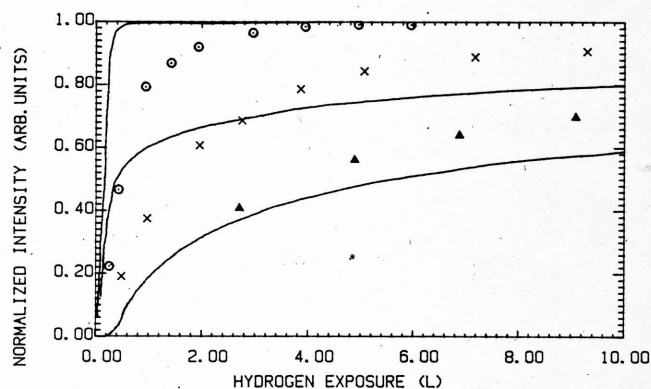


FIG. 1. Experimental photoemission intensities vs exposure in langmuirs (dots) and theoretical coverages (surface = θ_a and subsurface = θ_b) (solid lines) calculated by Dienes *et al.* using the kinetic equations of Lagos, Martinez, and Schuller (Ref. 2). The incident energy dependence of the photoemission intensity is clearly shown in comparing Smith's experimental data for $h\nu = 21.2$ eV (crosses) and 11.8 eV (triangles) at $P = 4.4 \times 10^{-8}$ Torr. It is important to emphasize that this energy dependence makes quantitative comparison with the kinetic equations difficult at present time. A comparison of the various curves at fixed energy ($h\nu = 21.2$ eV) gives an idea of the pressure dependence of the photoemission intensity.

Clearly, the photoemission data measures some weighted average of the hydrogen population of the first few layers. However, the specific way in which the weighting factors depend on photon energy (i.e., photon penetration) and population of the various layers is not clear yet. Since the photon beam only penetrates a few surface layers, the absorption in each one is significant. Therefore, the light intensity reaching the subsurface hydrogens (layer *b*) is reduced by the absorption in the chemisorption layer (layer *a*) by a factor dependent on the coverage θ_a . The normalized photoelectron intensity can therefore be written as

$$\frac{I}{I_0} = \sigma_a \theta_a + (1 - \sigma_a \theta_a) \sigma_b \theta_b,$$

where *I* is the photon intensity, *I*₀ is the incident intensity, and σ_a and σ_b are the photon capture cross sections by the *a* and *b* electron states. Equation (1) represents the simplest, linearized model possible. A detail calculation of σ_a and σ_b is complicated, however, it is clear that (a) the photoemission data points must lie between the curves θ_a and θ_b and (b) as the photon energy is lowered the photoemission curve must approach θ_a . The data of Strongin *et al.*^{2,10} and Smith¹¹ agree very well with the calculation of Dienes *et al.*¹ as far as these statements are concerned. We feel that further, quantitative comparisons are fruitless at present until the questions raised above are clarified both experimentally and theoretically.

There are several other problems with the analysis presented by Dienes *et al.*¹ which we will only mention very briefly. The data were fitted using parameters (several of them unspecified in the paper) from a different model (Pick's dilute phase model).⁹ Moreover, the initial slope of the curve $\theta_a(\epsilon)$ given by Dienes *et al.* is zero, which is in contradiction with the basic kinetic equations that predict a finite slope at the origin.² Our kinetic equations contain seven parameters. Adding σ_a and σ_b in order to make the

coverages comparable to photoemission data increases then to nine adjustable parameters. The fitting of an experimental curve with nine adjustable parameters is, in our opinion, of no use. For this reason our paper was written with a less ambitious purpose, to show the physical origin of the decoupling between surface and bulk.² In fact, the details of saturation, the existence of *one or various* subsurface layers, whether the sticking is of first or second order is immaterial as far as the qualitative conclusions are concerned; they only affect the details of the absorption curve.

In summary, the detailed comparison of the kinetic equations with the experimental hydrogen absorption curves as presented by Dienes *et al.* is erroneous mainly due to the lack of understanding of the photoemission data and an independent determination of the parameters in the problems. However, qualitative conclusions implying the decoupling of surface and bulk follow in a straightforward manner. For a proper comparison of experimental and theoretical absorption kinetics further work is needed in order to determine independently the parameters of the problem. In particular, the use of alternate surface spectroscopies, such as metastable atom deexcitation¹² which are more surface sensitive, could shed further light on the kinetics of hydrogen absorption in transition metals. We hope that this work will motivate further experimental and theoretical work in order to clarify the issues presented here.

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