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Reaction probability for exchange of hydrogen isotopes on palladium

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Surface conductances measured for the diffusion of hydrogen in palladium have been used to calculate the probability, as a function of temperature, pressure, and hydrogen isotope, that a H, D, or T atom will enter bulk Pd as a result of a collision of a H_2, D_2, or T_2 molecule with the Pd surface. This low probability is attributed to hydrogen penetrating a surface hydride phase under the driving force of the chemical potential of the gas consistent with the process having the exchange coefficient of the bulk material. These results were in good agreement with published experimental observations near 300 K and 100 kPa hydrogen pressure for D-H and H-D exchange. These exchange-probability calculations predict an isotope effect that inverts at elevated temperatures and, with decreasing temperature and increasing pressure, a marked decrease in the exchange probability.

INTRODUCTION

Foltz and Melius[1] have shown that even in the case of very active catalytic materials, i.e., palladium, the possibility that a hydrogen gas molecule will exchange with bulk hydrogen in palladium hydride is very remote with exchange probabilities, p_{H}, of the order of 2.6×10^{-7} near 300 K. Here p_{H} is the number of atoms exchanged with the palladium hydride per atom colliding with the surface. In this paper, the surface conductance determined by Powell and Kirkpatrick,[2] by experimentally treating the boundary-value problem of hydrogen diffusing in palladium, is used to calculate the probability, as a function of temperature, pressure, and hydrogen isotope, that a collision between a hydrogen molecule and the palladium surface will result in a hydrogen atom entering the bulk palladium, in agreement with the results of Foltz and Melius.[1] A palladium surface hydride phase observed by Powell, Kirkpatrick, and Conant[3] is invoked to explain why such small values of p_{H} are inherent properties of the palladium-hydrogen system and should not be particularly sensitive to whether the bulk phase is palladium metal or palladium hydride.

THEORY

The simplest solution to the boundary-value problem of diffusion, for the temporal and spatial dependence of the diffusing species, in a material is to change instantaneously the concentration of the diffusing species at the surface of the material from some value, usually zero, to a constant value, with the time of this change taken as $t=0$.[2,4] For gases dissolving in solids, this stepwise application of the boundary condition is achieved with a pressure change and the assumption that equilibrium is established across the gas-solid interface is invoked, allowing the calculation of the boundary-value concentration in the solid (C in units of mol m^{-3}) from the pressure of the gas (P in units of pascals). The resulting solution, independently of all geometrical considerations, yields an absorption rate, the rate of change of the volume integral of the concentration referred to hereafter as the uptake rate, that is infinite at $t=0$. This implies that every molecule striking the surface diffuses into the solid, i.e., $p_{\mathrm{H}}\approx1$. The next level of complexity added to this boundary-value problem is a boundary condition that restricts the flux of the diffusing species across a "film" at the gas-solid interface. This restricted flux is proportional to the concentration gradient across the film with the proportionality constant being the surface conductance (h in units of m s^{-1}). In this representation, the side of the bulk contacting the gas is at concentration C and the interface between the film and the bulk material is initially zero and increases in time as the difference between the flux through the film and the flux due to diffusion into the bulk solid. The resulting solution, independently of all geometrical considerations, yields an uptake rate that is linear at $t=0$. This implies that not every molecule striking the surface diffuses into the solid, i.e., $p_{\mathrm{H}}<1$. The simplest description of the film is that it has the same solubility as the bulk solid, but that it has a different diffusion coefficient (D_F) than that of the bulk solid (D in units of m^2 s^{-1}). If the film is of thickness L (in units of meters), then at $t=0$ the flux across the film is equal to $C\,D_F L^{-1}$ (in units of mol m^{-2} s^{-1}) and is also equal to Ch by definition, thus $h=D_F L^{-1}$. This is obviously somewhat artificial and a more experimentally achievable film would be a solid, similar to the bulk, having different values for the solubility, resulting in C_F as the concentration at the gas-solid interface, a concentration at the film-bulk interface corresponding to the same activity as the concentration (C) in the adjacent bulk material, and D_F for the diffusion coefficient in the film. Now $C_F D_F L^{-1}=Ch=F_F$, the limiting flux of diffusing species across the film, or $h=C_F D_F (CL)^{-1}$. In the most general case, the nature of the film is unknown, and the only physically meaningful quantity is F_F, with the separation of F_F into C and h a mere bookkeeping tool to relate the chemical potential of the gas to the bulk material in computationally meaningful units.

Lässer and Powell[5] measured the solubility of hydrogen isotopes in palladium yielding the following boundary condition for the diffusional uptake of hydrogen by palladium metal:

$$C_X=\rho_{\mathrm{Pd}}(K_X^{\infty}P_X)^{0.5}\frac{e^{-(\alpha-1)x_X}}{1-x_X}\,, \tag{1}$$

where ρ_{Pd} is the molar density of Pd, K_X^{∞} is the equilibrium constant for the dissolution of X in Pd, P_X is hydrogen pressure, x_X is concentration in terms of the $[X]/[\mathrm{Pd}]$ atom ratio ($C_X=\rho_{\mathrm{Pd}}x_X$), α is the activity parameter, and X=H, D, or T. K_X^{∞} and α are functions of temperature only. K_x^{∞} and, therefore C_X, are strongly hydrogen-isotope dependent.

Powell and Kirkpatrick[2] experimentally achieved the instantaneously stepwise boundary condition for a nearly perfect Pd sphere, found that the surface conductance boundary condition was necessary to describe the observations, and determined the surface conductance parameter to be

$$h=4.05e^{-(4995.3\ \mathrm{K})/T} \tag{2}$$

when C_{H} was taken to be given by Eq. (1). Within the experimental error, h was found to be independent of the pressure and hydrogen isotope.[2] Powell, Kirkpatrick, and Conant[3] demonstrated that the film was a "hydride" phase, having a stoichiometry of one atomic layer, that was more stable than $\mathrm{PdH}_{0.6}$ by ~6 kJ/mol H at temperatures near 298 K. This precludes the interpretation of the "film" by metal permeation concepts and leaves the interpretation of the maximum, i.e., limiting, flux (F_F) to the value of $C_{\mathrm{H}}h$, where C_{H} and h are both known as functions of temperature and pressure, but with only their product (F_F) having physical significance for the "film." Now the value for the maximum flux across a Pd surface for a particular hydrogen isotope has a half-power dependence on pressure, that of Eq. (1).

From the kinetic theory of gases, the flux of hydrogen molecules, f_X, colliding against the Pd surface is given by

$$f_X=P_X(2\pi M_X RT)^{-0.5}\,, \tag{3}$$

where M_X is the molecular weight of X_2, R is the gas-law constant, and T is the absolute temperature. Thus the reaction probability, i.e., the probability p_X, that a gas molecule-surface collision will result in a hydrogen atom penetrating the film to reach the bulk Pd is given by the ratio of the limiting flux, Eq. (1) times Eq. (2), to twice the gas flux, two times Eq. (3), since there are two X atoms per molecule. Foltz and Melius[1] referred to this flux of atoms onto the surface as the impingement rate. Now

$$p_X=\frac{C_Xh}{2f_X}=\rho_{\mathrm{Pd}}h\left[\frac{\pi M_X R K_X^{\infty} T}{2P_X}\right]^{0.5}\frac{e^{-(\alpha-1)x_X}}{1-x_X}\,. \tag{4}$$

RESULTS

Calculations of p_X (X=H,D,T) isotherms were carried out using Eq. (4) and are plotted in Fig. 1 as the dotted curves. The activity coefficient, the right-hand factor in Eq. (4) that is explicitly a function of x_{H}, results in C_{H}, thus p_{H}, being indeterminent at low temperatures and high pressures, i.e., pressures well above the "plateau" pressures for the formation of the bulk-hydride phase, consistent with the fact that the activity coefficient predicts transformation to form the bulk-hydride phase.[6] The dotted curves occur in the pressure-temperature field where palladium metal exists. At lower temperatures and higher pressures outside this field, i.e., the lower-right-hand corner of Fig. 1, and within the equilibrium context of Eq. (1); palladium can exist only as the hydride phase. The solid lines in Fig. 1 were calculated by setting $x_{\mathrm{H}}=0$, i.e., setting the activity coefficient equal to one, in Eq. (4). This was done based on the assumption that the film exists independently of whether the bulk material is Pd or $\mathrm{Pd}X_{0.6}$, and recognizes that the free energy of X in Pd and in $\mathrm{Pd}X_{0.6}$ (X=H,D,T) are approximately the same. The solid curves should represent the upper limit of the reaction probability for the exchange of hydrogen on palladium or palladium hydride within a factor of two or three. The upper limit refers to the fact that the probability calculated here considers only the process of hydro-

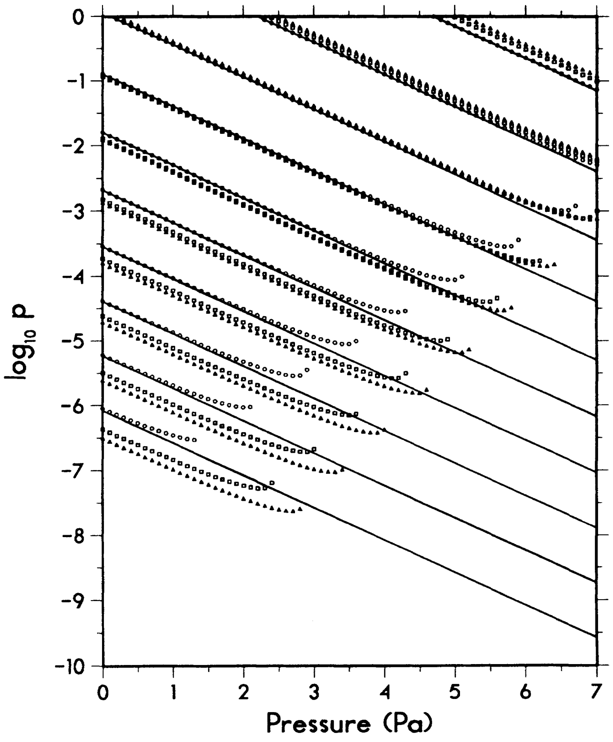

FIG. 1. Isothermal representation of p_{H}, the probability that a hydrogen atom in a hydrogen molecule colliding with a Pd surface will result in a hydrogen atom entering the bulk Pd. Points, isotherms calculated using exact values for C_X; circles, X=H; squares, X=D; triangles, X=T. Solid curves are calculated for H after setting the activity coefficient, the right-hand factor in (4), equal to one. Curves calculated for $1/T=0.0005$ K^{-1} (2000 K, upper curve), 0.0010 K^{-1}, 0.0015 K^{-1}, 0.0020 K^{-1}, 0.0025 K^{-1}, 0.0030 K^{-1}, 0.0035 K^{-1}, 0.0040 K^{-1}, 0.0045 K^{-1}, 0.0050 K^{-1} (200 K, lower curve).

gen crossing the palladium surface from the gas phase to the bulk phase and does not include the reverse process necessary to complete the exchange. The factor of two or three refers to the uncertainty introduced by the assumption that the chemical potential of hydrogen isotopes in palladium and palladium hydride are the same. This assumption is within the general accuracy range of p_{H} reported by Foltz and Melius[1] of approximately a factor of 2. For the temperature range of 200–400 K, the solid lines in Fig. 1 can be empirically described by the following Arrhenius relationships:

$$p_{\mathrm{H}} = 286 P_{\mathrm{H}}^{-0.5} e^{-(3935\ \mathrm{K})/T} , \tag{5a}$$

$$p_{\mathrm{D}} = 360 P_{\mathrm{D}}^{-0.5} e^{-(4120\ \mathrm{K})/T} \tag{5b}$$

$$P_{\mathrm{T}} = 441 P_{\mathrm{T}}^{-0.5} e^{-(4223\ \mathrm{K})/T} \tag{5c}$$

where P_{H} is in pascals. Calculations using Eqs. 5(a)–5(c) for 298 K and 100 kPa, 25 °C, and 1 atm, yielded values of $p_{\mathrm{H}} = 1.7 \times 10^{-6}$, $p_{\mathrm{D}} = 1.1 \times 10^{-6}$, and $p_{\mathrm{T}} = 1.0 \times 10^{-6}$ that are only slightly greater than the value of 0.26×10^{-6} reported by Foltz and Melius.[1]

DISCUSSION

The exchange probability for gaseous hydrogen isotopes reacting with palladium or palladium hydride, 6 orders of magnitude less than unity, has been determined within an order of magnitude, from a simple extension of hydrogen surface conductance measurements of pure hydrogen isotopes in palladium metal to that for palladium hydride using the known surface hydride phase to explain the existence of the film, that limits the flux of hydrogen across the surface; and using the similarities between the chemical potential of hydrogen in palladium and in palladium hydride to explain the similar driving force for hydrogen penetrating the film. This supports the observations of Foltz and Melius[1] and explains their observations as an inherent property of the palladium-hydrogen system. The exchange reaction cannot, however, be postulated as a simple second-order reaction[1] between a gas molecule and a surface species. The exchange reaction is instead a second-order reaction between the gas molecule and the entire palladium surface that drives a hydrogen through the surface hydride film into the bulk palladium or palladium hydride. With the exception that these surface reactions are in total inefficient, the particulars of dissociation of hydrogen on the surface and migration of hydrogen through the film are not determined. This does not change the general form of the kinetic model[1] used to determine the exchange probability, since the process is still surface-area dependent. However, the penetration of the reacting hydrogen into the bulk phase is a particularly important feature since the separation factor used by Foltz and Melius[1] is that of bulk palladium hydride. The surface hydride film was found to have a much smaller isotope effect,[3] thus a much smaller separation factor, than that used in the isotope-exchange model.[1] On the other hand the separation factors for hydrogen isotopes in palladium and in palladium hydride are very similar, with that for palladium hydride being slightly greater.[7,8]

An interesting feature of this phenomenon is the inverse half-power pressure dependence of the reaction probability. The inverse half-power pressure dependence of the flux is consistent with the dissociation of H_2 molecules being required to achieve the flux. The efficiency with which gas molecules may react to penetrate the surface film for a given collision diminishes with increasing pressure. As the pressure decreases below 1 Pa, the surface phase (i.e., the film) transforms from a surface palladium hydride phase to a surface palladium phase depleting the surface of hydrogen.[3] In the < 1 Pa pressure range, the bulk palladium metal phase is essentially depleted of hydrogen. Below 10 mPa, the range of high-vacuum surface analysis, the hydrogen-palladium reactions are true surface reactions in which the gas-solid reaction has a reaction probability that is very near unity and with the bulk palladium serving a minor role as a sink for hydrogen at very low concentrations. This is the pressure domain studied in high-vacuum surface analysis experiments,[9–12] where the residence time and structure of hydrogen on the surface is evidence for a surface phase. It is indeed interesting that the surface phase transformation from metal to hydride switches this system between a classical gas-surface reaction domain and a gas-bulk-solid reaction domain over a decade-wide pressure range beginning just above the upper pressure limits for the operation of most surface analysis techniques. The surface conductance[2] and surface hydride[3] experiments were carried out using thermal cycling in hydrogen and oxygen as the surface cleaning step without explicit proof that the surfaces were free of other molecular species during these experiments. Surface impurities can contribute to reducing the surface conductance[2] and that surface impurities contribute to the character of the surface hydride film cannot be explicitly disregarded. Given the high purity of the gases used in the surface conductance and surface film experiments and in the absence of a viable technique for passively monitoring in real time the surface of the palladium for impurities such as carbon monoxide and sulfur at pressures above 1 Pa, the role impurities played in these experiments[2,3] is assumed to be an inherent and reproducible property of the film. For pressures above 1 kPa, it is inconceivable that gas-borne impurities are not available in monolayer quantities. The isotope effect at constant pressure for this reaction probability is also interesting in that it inverts at elevated temperatures. This inversion results from the isotope effect, in the limiting flux due to surface conductance, approaching unity, i.e., no isotope effect, at very high temperatures; whereas the isotope effect for the gas flux is independent of temperature and depends only on the ratio of the square roots of the molecular weights of the isotopic species considered.

CONCLUSIONS

The low reaction probability for hydrogen-isotope exchange over palladium hydride has been explained as an inherent property of the palladium-hydrogen system whereby a surface hydride phase (i.e., "film") forms near 1 Pa pressure and this limits the flux of hydrogen between the gas and bulk phases. This description, based on a straightforward interpretation of the experimental solution to the diffusion-with-surface-conductance boundary-value problem, predicts a decreasing reaction probability with increasing pressure and decreasing temperature, and an isotope effect that inverts at elevated temperatures. It also demonstrates why the separation factor for this model is that for bulk palladium or palladium hydride. Little can be concluded about transport mechanisms in the film itself other than the observation that the cumulative process of hydrogen gas adsorption, dissociation, and diffusion through the film is inefficient.

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