JOURNAL OF CATALYSIS **108**, 409–425 (1987)

Studies of Isotopic Exchange between Gaseous Hydrogen and Palladium Hydride Powder

G. W. FOLTZ AND C. F. MELIUS

Sandia National Laboratories, Livermore, California 94550

Received May 8, 1986; revised July 30, 1987

A gas flow apparatus has been constructed and used to study the isotopic exchange reaction occurring between the solid and gas phases in hydrogen (deuterium) gas flows directed through packed-powder beds of β-phase palladium deuteride (hydride). Spontaneous Raman light scattering is employed to obtain a real-time analysis of the isotopic composition of the gas (H_2, D_2, HD) exiting from the bed. A parametric rate-equation model is described which depicts the time-dependent behavior of the isotopic exchange process. The exchange mechanism is assumed to be rate-limited by processes occurring on the surface of the powder. The fundamental kinetic parameter of the model is the isotopic exchange probability, p, which is the probability that an isotopic exchange event occurs during a collision of a gas-phase atom with the surface. Isotope effects between the gas and solid phases are explicitly included in terms of the isotope separation factor, α. Results of the model are compared with the experimental measurements and, using a literature value of $\alpha = 2.4$, good agreement is obtained for $p \approx 10^{-7}$. In view of the importance of the isotope effects in the hydrogen/palladium system and the range of α values reported for the β-phase in the literature, the sensitivity of the model results to a variation in the value of α is examined.

INTRODUCTION

Isotopic exchange of an element between the gas phase and a solid containing that element (variously called heterophase, heterogeneous, or interphase exchange) represents a fundamental gas–solid interaction. The overall process depends, in general, upon both the thermodynamics and the kinetics of the reactions of the isotopes at the surface of the solid and of the diffusion of the isotopes throughout the solid (*1, 2*). Depending upon the gas–solid system and the conditions under which it is examined, differences in behavior between the isotopes in the solid and in the gas (isotope effects) can be significant. Studies of this exchange process have been reported for a wide variety of gas–solid systems. Examples range from what may be termed fundamental processes, such as the exchange between gaseous oxygen and solid oxides (*3*) and the exchange between gaseous hydrogen and solid hydrides (*2, 4–10*), to processes in which the exchange occurs between chemically complex gases and solids [see, for example, (*2, 10, 11*)]. Further distinction can be made regarding the nature of the solid-state phase involved and whether the solid composition is stoichiometric or nonstoichiometric. In addition to the study of the basic exchange mechanism itself, other issues addressed in the literature include the relationship between the exchange interaction and the catalytic activity of the solid, and the use of the exchange process (a) to determine isotope mobility at the surface and in the solid, (b) to measure the amount of an isotope originally contained in the solid, and (c) for isotope separation. Several kinetic models have been presented for closed reaction systems (*2, 4, 12*).

The purpose of this paper is to present the results of an investigation of hydrogen (deuterium) exchange between the solid and gas phases in hydrogen (deuterium) gas flows through a packed-powder bed of

0021-9517/87 $3.00

β-phase palladium deuteride (hydride). The hydrogen–palladium hydride system is of considerable importance in that palladium is widely used as a catalyst for reactions involving hydrogen (hydrogenation and dehydrogenation, for example). The metal readily sorbs hydrogen and the presence of this hydrogen in the metal can significantly affect the catalytic properties of the solid (*13*). Furthermore, palladium is often employed in both studies of and systems for hydrogen isotope separation.

The techniques used in the experimental investigation of gas–solid exchange interactions may be classified (*2*) according to (a) whether the system is closed or open (i.e., the overall isotopic composition of the gas plus solid system is fixed or varying, respectively) and (b) the initial conditions employed which may in turn determine the variety of processes that occur during the experiment. An important point regarding the latter consideration is the extent, if any, to which net gas sorption accompanies the exchange process. In the present work, an open experimental configuration is employed in which one isotope is initially sorbed into the palladium powder and the other isotope is subsequently flowed through the powder. Using spontaneous Raman light scattering, time-resolved measurements of the gas composition exiting from the bed during the exchange process are obtained. A theoretical model, in which a gas-to-solid isotope effect is incorporated, is used to interpret these measurements in terms of a surface-rate-limited reaction process. Comparison of the model and experiment results yields an isotopic exchange probability for the process.

Andreev and co-workers (*5, 8–10*) have studied hydrogen isotope exchange between gaseous hydrogen and palladium hydride under a variety of conditions using palladium black. In general, isotopic exchange rate constants were measured and various pressure and temperature dependences of these constants were determined. Also included (*9*) are the effects on the exchange kinetics of the dispersal of the palladium on alumina supports. Sicking *et al.* (*2*) have examined the kinetics of the exchange of hydrogen and trace levels of tritium between the gas phase and palladium, analyzing their results using rate equations valid for small values of the [T]/[H] ratio. Mention should also be made here of studies of gas-phase hydrogen isotope equilibration (homophase exchange) over palladium in which the effects of hydrogen sorbed into the metal are examined (*14, 15*).

METHOD—EXPERIMENT

The apparatus used for the present measurements is shown schematically in Fig. 1. Prior to the running of an exchange experiment, the gas flow channel is evacuated via an attached high-vacuum pumping unit and the palladium powder bed is baked out under vacuum. A known quantity of either hydrogen or deuterium is then sorbed into the powder. Subsequent to this preparation, the fast-acting, high-conductance valves are opened, allowing the other isotope, deuterium or hydrogen, respectively, to flow through the powder from the input on the left to the exhaust on the right. Optical access to the gas flow allows real-time analysis of the isotopic composition of the gas (H_2, D_2, HD) exiting from the powder bed to be performed by means of (gas-phase) spontaneous Raman light scattering. In addition, real-time gas pressure and flow rate measurements are made of the flow simultaneously with the composition measurements.

Flow Channel and Powder Bed

The flow channel is of modular design with all major components fabricated from stainless steel and joined together with metal seals. The channel has cylindrical symmetry and the central portion, containing the powder bed, optical access section, and pressure transducer ports, is 1.0 cm in diameter. Care has been taken in the design

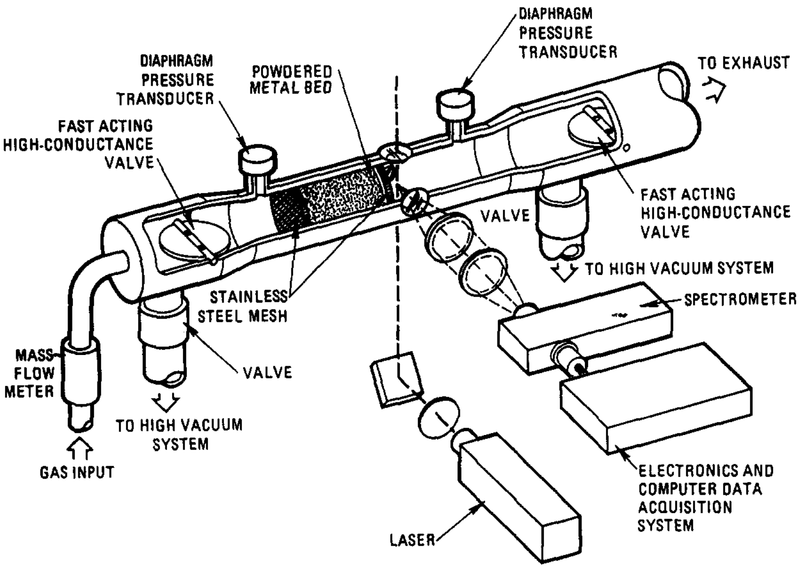

FIG. 1. Schematic diagram of hydrogen isotope exchange apparatus.

of this portion of the channel to minimize regions (outside of the powder bed) where gas eddies in the flow could occur and thereby distort the gas composition measurements.

The powder bed consists of a 20.3-cm-long section of the flow channel filled with quasi-spherical palladium powder obtained from D. F. Goldsmith Chemical & Metal Corp.[1] A chemical analysis of the palladium provided by the vendor indicates the presence of the following trace elements: Ag, Al, Au, Bi, Co, Cr, Cu, Fe, Ir, Mg, Mn, Mo, Ni, Pb, Pt, Si, Sn, and Ti, with Al being the most prominent impurity. In an ICP analysis of "as-received" powder, performed at Sandia National Laboratories, metal impurities were detected as follows, where amounts in weight percentages are given in parentheses: Al (0.0692), Ni (0.0148), Ag (0.0105), Cu (0.0078), K (0.0020), and Mg (0.0016). An electron microprobe analysis of "as-received" powder, done at Sandia, revealed ≤ 0.2 wt.% aluminum distributed throughout the solid, as well as small (≤ 5 μm) alumina inclusions in the solid and nodules on the particle surfaces. Aluminum and oxygen, at ~15 and ~10 atomic percent levels, respectively, have been detected on the surface of the "as-received" powder by Auger electron spectroscopy (AES) at Sandia. The AES results further imply that the surface aluminum is present partly in metallic form and partly in conjunction with oxygen as alumina.

The powder is sieve-sized, so that particle diameters lie in the interval 106–124 μm, and is then pour-packed into the bed section with some tapping on the side of the container. The powder is retained in the channel by stainless steel wire mesh with nominal and absolute filtration ratings of 30 and 55 μm, respectively. A packing or bulk density of 7.5 gm/cm^3 is obtained, corresponding to an average void fraction or porosity, ϕ, of 0.38. Metallographic examination of the powder indicates a negligible amount of internal void volume within the individual powder particles. Therefore, the porosity is assumed to be interconnected. The value of 0.38 agrees well with the results of studies of poured random packing

---

[1] D. F. Goldsmith Chemical & Metal Corp., 909 Pitner Ave., Evanston, IL 60202.

and close random packing of spheres in which the mean porosity ranged between 0.375 and 0.391 in the former type of packing, and the minimum porosity ranged between 0.359 and 0.375 in the latter type (*16*). An estimate of the specific surface, S_o, of the bed (powder surface area per unit solid volume) can be made by assuming the powder particles to be smooth spheres of fixed diameter, d. Under such conditions, S_o equals the surface-to-volume ratio of the spherical particles, which is given by $6/d$. In the present case, using $d = 115\ \mu\text{m}$, $S_o = 522\ \text{cm}^{-1}$. A specific surface this small (equivalent to 0.004 m^2/g Pd) is difficult to measure by conventional gas adsorption methods such as the BET technique; however, measurements of S_o using the pressure/flow characteristics of gas flowing through the bed along with the Carman–Kozeny equation (see below) yield results in quite good agreement with the geometric value given above. Aside from sieve-sizing, the powder is loaded into the bed "as received" from the vendor. A preliminary cleaning of the powder *in situ* is performed by flowing hydrogen through the bed as a reducing agent and then by hydriding the powder at a gas overpressure of ~1 atm at least once before any experiments are conducted. Each bed is used for several exchange experiments.

The initial hydriding or deuteriding of the powder prior to an exchange experiment is accomplished in a controlled fashion by admitting a measured amount of gas (over a period of several hours) into an evacuated portion of known volume of the flow channel which contains the powder. By measuring the gas pressure over the powder (gas overpressure) after equilibrium has been reached, the stoichiometry of the resulting solid, PdH_x or PdD_x, may be determined. For the initial conditions used in the present experimental work, room temperature and an overpressure of just above local atmospheric pressure, x is found to be about 0.65 and 0.61 for the PdH_x and PdD_x solids, respectively, which corresponds to the β-phase in both cases.[2] The relative difference between these two values is in reasonable agreement with results reported in the literature (*15, 17, 18*) while, on an absolute scale, the values appear to be about 5–10% low. This latter result may be attributable to the metal impurity levels in the powder (*17, 18*). Because of the mechanical constraints of the powder containment, the ~10% increase in the volume of the solid which accompanies hydriding (deuteriding) pure palladium into the β-phase (*17–19*) is assumed to result in a reduction in both the porosity of the bed (by ~17%) and in the specific surface of the bed (by ~3% in the spherical particle approximation). Repeated hydriding (deuteriding) of the powder (usually followed by isotope exchange) has, to date, caused no statistically significant difference from run to run in the initial stoichiometry of the hydride (deuteride). SEM pictures of the (dehydrided) powder taken following repeated hydriding (deuteriding) show that some change in the surface morphology of the particles has occurred; however, AES examination of this powder does not indicate any significant change in the surface composition as compared to the "as-received" powder.

Absolute capacitance manometers held at a controlled temperature of 318 K are used to measure, independently of composition, the total pressure of the gas entering, P_{in}, and leaving, P_{out}, the bed. A mass flow meter, located at the input end of the flow channel (see Fig. 1), where it is exposed to only the input gas type, is used for volumetric gas flow rate, Q, measurements. The

---

[2] For the purposes of the exchange experiments described here, it is not necessary for the gas–solid system to be in true equilibrium as long as the gas overpressure is measured just before the exchange process is initiated (allowing the hydrogen or deuterium content in the powder to be determined). However, considering the time constraints of the hydriding procedure and the small room temperature fluctuations, the values of x reported above are believed to be representative of a near-equilibrium situation.

flow meter is periodically calibrated against a wet test flow meter under conditions simulating those of an experiment. The fast-acting, high-conductance valves, the opening of which initiates the gas flow and defines $t = 0$ of the experiment, are pneumatically operated butterfly valves. The time interval required for these valves to open (~1 s) is negligibly short compared to the time scale involved in the exchange process under the present experimental conditions. High-purity gases (99.9995% pure H_2 and 99.99% minimum pure D_2) are used "as received" from the vendor.

In all experimental work reported in this paper, the gas exits from the bed at (essentially) local atmospheric pressure ($= P_{\text{out}}$), while the input gas pressure, P_{in}, is set positive with respect to P_{out}, typically in the range 1050 to 1200 torr (all pressures given are absolute; 1 torr = 133.3 N/m^2), to drive the gas flow through the bed. For hydrogen flowing through a hydrided bed, the resulting values of the gas flow rate, Q, lie between 0.6 and 1.1 standard liters/min (slm; 1 slm = 0.0000167 m^3/s at standard conditions of 760 torr and 0°C), while somewhat lower flow rates result for deuterium flowing through a deuterided bed because of the greater viscosity of deuterium. The measured input pressure and flow rate values are observed to change somewhat over the course of an exchange experiment as a result of the changing composition, and therefore viscosity, of the gas flowing through the bed. The pressure/flow characteristics of the bed can, to a reasonable extent, be described by Darcy's law, which states that the volumetric flow rate at the mean pressure in the bed is proportional to the pressure drop, $(P_{\text{in}} - P_{\text{out}})$, across the bed. The proportionality constant is given by $KA/\mu L$ where K is the (specific) permeability of the bed, μ is the viscosity of the gas, and A and L are the cross-sectional area and length of the bed, respectively. K in turn depends on the porosity and specific surface of the bed and may be expressed according to the Carman–Kozeny theory as $K = \phi^3/[c(1 - \phi)^2 S_0^2]$, where c is a constant (*20*). (Subsidiary experiments indicate that the presence of the mesh used to contain the powder in the bed has a negligible effect on the pressure/flow characteristics of the bed.)

The flow channel is attached to a high-vacuum pump stand consisting of a turbomolecular pump backed by a zeolite-trapped mechanical pump. Base pressures attained near the ends of the powder bed at room temperature are estimated to be in the 10^{-7} torr range. Prior to each exchange experiment, the flow channel is evacuated and the powder bed is heated under vacuum to a temperature around 475–500 K. A residual gas analyzer is used to help ensure that the initial vacuum conditions for an experiment are similar from run to run.

Raman Light Scattering

The optical access section of the flow channel lies immediately "downstream" from the powder bed and consists of four uncoated, fused silica windows set at right angles to each other azimuthally around the flow channel at the same axial location along the channel. The windows are conically shaped, having a clear aperture of 1.2 cm externally and 0.3 cm internally (see Fig. 1). This design allows *f*/1.7 optical efficiency while minimizing perturbations by the windows on the gas flow. High-temperature elastomer O-rings are used for the window seals.

Raman light scattering is used for analyzing in real time the isotopic composition of the gas exiting from the bed. This technique provides *in situ* measurements, thereby eliminating the need to extract sample gas from the flow. The 514.5-nm output of an argon ion laser is directed vertically through the flow channel at right angles to the gas flow (see Fig. 1). The laser beam is brought to a focus on the central axis of the flow tube. A fraction of the light which is Raman scattered at ~90° out of the laser focal volume by molecules in the flow is collected and directed through a colored glass filter, to aid in rejecting elastically scattered laser light, and then into a 0.5-m single-grating spectrometer. The spectrometer is tuned to select the wavelength component of the scattered light corresponding to the isotope of interest, and this light is then detected at a cooled photomultiplier tube using standard photon counting techniques.

The specific Raman interaction observed corresponds to the (integrated) Q-branch ($\Delta J = 0$) of the $v = 0$ to 1 ro-vibrational transition in the ground electronic state of H_2, D_2, or HD. At the temperatures involved in the present work (~300 K), most of the H_2, D_2, and HD molecular populations lie in their lowest few rotational states in the $v = 0$ vibrational states of their ground electronic states. The exit slit of the spectrometer is opened sufficiently wide to integrate onto the photomultiplier tube the Q-branch Raman signals arising from these (lower) rotational populations of a given molecular species. (The fact that Q-branch Raman signals resulting from several less-populated, higher-lying, quantum states of a molecule are not collected is not a problem as long as no significant temperature changes occur in the gas during the experiment. In the present case, a temperature change of 25 K would produce, at most, a 2% change in the detection sensitivity.) As a result of the large vibrational Raman shifts in H_2, D_2, and HD, and the large isotope shifts between these molecules, the ro-vibrational Raman signals from the different molecular isotopes are, in terms of frequency, both well-removed from the elastically scattered laser light and well-separated from each other. These features permit unambiguous species detection. Furthermore, the large cross section for ro-vibrational Q-branch Raman scattering which hydrogen possesses allows for good species detectability.

The Raman signal arising from a given isotope in the gas flow is converted to the absolute partial pressure of that isotope in the flow by means of a calibration signal obtained from a known pressure of the isotope in the flow channel. Although single-channel detection (i.e., one isotope at a time) is employed, the time scales for exchange involved in the present experiments allow the spectrometer to be manually multiplexed between the various isotopes during the exchange process. Only two of the three species need be directly detected as subtraction of the sum of the resulting partial pressures of these two species from the total output pressure, P_{out}, determines the partial pressure of the third species. Typically, H_2 and D_2 are chosen for direct detection since calibration signals are most easily obtained for these species. (The existence of HD in the gas flow during the exchange process has, however, been confirmed using Raman light scattering.)

Using a modest laser power of ≤ 1 W and a signal integration time of 1 s, a partial pressure detection limit of 5 to 10 torr is achieved. This limit results principally from the dominant noise source, which is laser light elastically scattered from the surfaces of the windows and flow channel.

METHOD—MODEL

Rate Equations

The results of the experiments described above are analyzed with a parametric rate equation model in which both the effects of isotopic exchange and gas flow through the bed are included. For specificity, the model is described for the case in which deuterium is initially sorbed into the bed and hydrogen gas flowed into the bed. (Applying the model to the reverse situation of deuterium flowing into a palladium hydride bed poses no additional problems.)

While hydrogen and deuterium are present both as atoms (in the solid) and molecules (in the gas), the rate equations are written solely in terms of atomic densities of H and D. Letting n_{s_D}, n_{s_H}, n_{g_D}, and n_{g_H} represent the densities in moles of deuterium and hydrogen atoms per unit volume in the solid and gas phases, respectively, four coupled rate equations (one for each phase and isotopic species) describing the overall macroscopic aspects of the exchange process may be written as

$$\text{Solid: } \partial n_{s_D}/\partial t = -R \qquad (1a)$$

$$\partial n_{s_H}/\partial t = R \qquad (1b)$$

$$\text{Gas: } \partial n_{g_D}/\partial t = (1 - \phi)R/\phi - \partial(n_{g_D}v_f)/\partial x \qquad (2a)$$

$$\partial n_{g_H}/\partial t = -(1 - \phi)R/\phi - \partial(n_{g_H}v_f)/\partial x. \qquad (2b)$$

Equations (1a) and (1b) simply define R, the isotopic exchange rate; Eq. (1a) describes the loss rate of the initially sorbed isotope, deuterium, from the solid into the gas due to the exchange interaction, while Eq. (1b) equates this deuterium loss rate to the rate of gain by the solid of hydrogen from the gas. The net sorption of gas during the exchange is, therefore, assumed to be zero. Equations (2a) and (2b) give the time rate of change of the gas-phase deuterium and hydrogen concentrations. The first term in Eq. (2a) reflects the deuterium loss from the solid as the appearance of that isotope in the gas phase. The factor $(1 - \phi)/\phi$ in this term is the solid-to-void volume ratio of the bed and adjusts for the difference between solid volume and void volume in the bed. The second term in Eq. (2a) accounts for the fact that the gas is flowing through the bed and comes from the fluid dynamic equation of continuity written for one-dimensional flow, where x is measured axially through the bed and v_f is the flow velocity along that dimension. Equation (2b) for gas-phase hydrogen is identical to Eq. (2a) except for the minus sign in front of the R term which represents the loss of H atoms from the gas to the solid.

Isotopic Exchange Rate

In order to specify the nature of the isotope exchange rate, R, it is necessary to examine the microscopic aspects of the exchange process. The overall exchange reaction comprises of several more elementary processes involving the hydrogen and deuterium atoms and molecules which can be conveniently separated into three groups: processes occurring within the solid, surface processes, and gas-phase processes occurring in the flowstream. The solid-phase processes can include, for example, solid diffusion, grain boundary diffusion, and trapping, which determine the transport of sorbed hydrogen and deuterium atoms in the solid. The gas-phase processes can include diffusion, turbulent transport, and boundary-layer processes, which govern the motion of the gas molecules between the flowstream and the particle surface. Finally, the surface processes can include the various adsorption and desorption processes, and movement of species on the surface, which constitute the chemical exchange mechanism itself. Previous work (*21*) has indicated that, for the present experimental conditions, the solid- and gas-phase processes occur on a time scale which is short compared to that of the surface processes and, therefore, that the group of surface interactions constitutes the rate-limiting step of the overall exchange reaction. Consequently, in the evaluation of R, both solid- and gas-phase processes are assumed to proceed with sufficient rapidity so as to have a negligible effect on the exchange kinetics; the main modeling effort is directed at the surface processes. The ultimate validity of such a surface-rate-limited model is, of course, determined by comparison with experiment.

It is not necessary to choose a specific surface reaction mechanism in order to give a description of the reaction kinetics at the surface. A general set of exchange reactions may be written (for zero net gas sorption during the exchange) as

$$D_2 + H_s \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} HD + D_s \qquad (3a)$$

$$HD + H_s \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} H_2 + D_s, \qquad (3b)$$

where D_2, HD, and H_2 are gas-phase molecules above the surface, while H_s and D_s represent hydrogen and deuterium atoms, respectively, bound to the solid (see also Discussion). With the rate constants for the reactions denoted as indicated by the k_i's in Eqs. (3a) and (3b), the rate equation for the concentration of D_s is

$$\partial[D_s]/\partial t = k_1[D_2][H_s] + k_2[HD][H_s] - k_{-1}[HD][D_s] - k_{-2}[H_2][D_s], \quad (4)$$

where the square brackets indicate concentrations of the species enclosed. Assuming that the following relationships hold between the k_i's,

$$k_2 = \tfrac{1}{2}k_1 \quad (5a)$$

$$k_{-1} = \alpha k_2 = \tfrac{1}{2}\alpha k_1 \quad (5b)$$

$$k_{-2} = \alpha k_1, \quad (5c)$$

where the factor of $\frac{1}{2}$ in Eq. (5a) is obtained from statistical considerations and where a gas-to-solid-phase isotope effect is explicitly taken into account by the use of the isotope separation factor, α, Eq. (4) can be expressed as

$$\partial[D_s]/\partial t = k_1\{([D_2] + \tfrac{1}{2}[HD])[H_s] - \alpha([H_2] + \tfrac{1}{2}[HD])[D_s]\}. \quad (6)$$

Letting f_{g_H}, f_{g_D}, f_{s_H}, and f_{s_D} equal the mole fractions in the gas and solid phases of H and D, respectively, such that

$$f_{g_H} = ([H_2] + \tfrac{1}{2}[HD])/([H_2] + [HD] + [D_2])$$

$$f_{s_H} = [H_s]/([H_s] + [D_s])$$

and similarly for deuterium, and letting $\bar{k}$ be the averaged or isotope independent rate constant $[\bar{k} = (k_1k_{-2})^{1/2}]$, Eq. (6) can be rewritten as

$$\partial[D_s]/\partial t = \bar{k}([H_2] + [HD] + [D_2])([H_s] + [D_s]) \{(\alpha)^{-1/2}f_{g_D}f_{s_H} - (\alpha)^{1/2}f_{g_H}f_{s_D}\}. \quad (7)$$

Up to this point the exact nature of both the k_i's and the species concentrations has been left unspecified. The system has simply been divided into a gas-phase region, a solid-phase region, and an interfacial region separating the gas and the solid. Identification of the species concentrations as surface densities, as is pertinent for a strict surface reaction, may be accomplished in Eq. (7) by regarding ($[H_s]$ + $[D_s]$) as the surface density, N_{surf}, of hydrogen and deuterium atoms bound to the solid, i.e.,

$$N_{surf} = ([H_s] + [D_s]), \quad (8)$$

and by associating ($[H_2]$ + [HD] + $[D_2]$) with the flux or impingement rate, I, onto the surface of all gas-phase species. I can be expressed as

$$I = \tfrac{1}{4}(n_{g_D} + n_{g_H})(8RT/\pi M)^{1/2}, \quad (9)$$

where $(8RT/\pi M)^{1/2}$ is the thermal velocity, v_t, of a gas molecule of mass M at temperature T and R is the gas constant. Note that, as a result of the assumption that the transport processes in the gas and solid phases are rapid compared to the interfacial processes, this correspondence of species concentrations with surface densities does not create any ambiguity in the definitions of the mole fractions, f_i. Under this assumption, the [H]/[D] ratio in the near-surface gas phase is proportional to the [H]/[D] ratio out in the free-stream gas and, similarly, the [H]/[D] ratio on the solid surface is proportional to that ratio deep in the solid. Thus, from Eqs. (1), (7), (8), and (9),

$$R = \tfrac{1}{4}k(n_{g_D} + n_{g_H})(8RT/\pi M)^{1/2}S_o N_{surf} \{(\alpha)^{1/2}f_{g_H}f_{s_D} - (\alpha)^{-1/2}f_{g_D}f_{s_H}\}, \quad (10)$$

where the constant of proportionality, k, is the isotopic exchange coefficient and the inclusion of the specific surface, S_o, converts the exchange rate from moles per second per unit solid surface area to moles per second per unit solid volume as required by Eqs. (1) and (2). The values of the f_i's obtained from volume species densities are used in the model computations and the proportionality constants mentioned above concerning the [H]/[D] ratios are absorbed into the isotopic exchange coefficient.

With R given by Eq. (10), Eqs. (1a) and

(1b) indicate that deuterium is lost from and hydrogen gained by the solid when $(\alpha)^{1/2}$ times the product of the hydrogen impingement rate [given by $\frac{1}{4}(n_{g_D} + n_{g_H})v_t f_{g_H}$] and the deuterium surface density [given by $N_{surf} f_{s_D}$] is greater than $(\alpha)^{-1/2}$ times the product of the deuterium impingement rate [given by $\frac{1}{4}(n_{g_D} + n_{g_H})v_t f_{g_D}$] and the hydrogen surface density [given by $N_{surf} f_{s_H}$]. If this inequality is reversed then hydrogen is lost from and deuterium gained by the solid. At equilibrium,

$$\{(\alpha)^{1/2} f_{g_H} f_{s_D} - (\alpha)^{-1/2} f_{g_D} f_{s_H}\} = 0$$

and

$$\begin{aligned}\alpha &= (f_{s_H}/f_{g_H})/(f_{s_D}/f_{g_D}) \\ &= (f_{g_D}/f_{g_H})/(f_{s_D}/f_{s_H}), \quad (11)\end{aligned}$$

as required according to the standard definition of the isotope separation factor [see, for example, Ref. (*1*)]. Note that the presence of α in general removes the symmetry otherwise present between the f_i concentration terms in Eq. (10) and, depending upon its value ($\neq 1$), drives the equilibrium of the exchange reaction away from the condition in which, for each isotope, the gas- and solid-phase mole fractions are equal. In the case of the H/D/Pd system, $\alpha > 1$, indicating that hydrogen has a greater affinity for the metal than deuterium relative to the gas phase. Therefore, the direction of the exchange reaction which results in hydride is favored over the reverse direction which leads to the deuteride.

Isotopic Exchange Probability

From Eqs. (1) and (10) it is seen that the isotopic exchange coefficient, k, has units of cm^2/mol. It is therefore useful to express k as

$$k = p\sigma, \quad (12)$$

where σ is defined as the surface area occupied by a mole of adsorbed H or D atoms such that $\sigma = (N_{surf})^{-1}$. The quantity p can then be interpreted as the probability that an isotopic exchange event occurs during a collision of a gas-phase atom with the surface. Thus, p is called the isotopic exchange probability and it constitutes the fundamental kinetic parameter of the model. The temperature dependence of p can be included explicitly via an Arrhenius equation

$$p = p_0 \exp(-E_a/RT), \quad (13)$$

where E_a is an activation energy for the exchange reaction.

Gas-Phase Molecular Composition

At any location in the bed and at any time, conversion of the gas-phase atomic densities of H and D to molecular densities of H_2, D_2, and HD is accomplished assuming that equilibrium between the isotopic molecular species in the gas holds at all points in space and time within the bed. The process which establishes this equilibrium among the gas-phase species can be described by the reaction

$$H_2 + D_2 \rightleftarrows 2HD. \quad (14)$$

The equilibrium constant, K_{eq}, for this reaction is given by (*22*) as

$$\log K_{eq} = -(155/4.57T) + 0.6276 \quad (15)$$

and has a value of 3.267 at 299 K. The molecular mole fractions, $f_{g_{HD}}$, $f_{g_{H_2}}$, and $f_{g_{D_2}}$, are given in terms of the atomic mole fractions, f_{g_H} and f_{g_D}, and K_{eq} by

$$\begin{aligned}f_{g_{HD}} &= -[K_{eq}/(4 - K_{eq})] \\ &\quad + [2/(4 - K_{eq})]\{(K_{eq}^2/4) \\ &\quad\quad + 4K_{eq}[1 - (K_{eq}/4)]f_{g_H} f_{g_D}\}^{1/2} \\ f_{g_{H_2}} &= f_{g_H} - \tfrac{1}{2} f_{g_{HD}} \quad (16) \\ f_{g_{D_2}} &= f_{g_D} - \tfrac{1}{2} f_{g_{HD}}.\end{aligned}$$

Implementation

In applying the model to the experimental situation, the set of coupled partial differential equations, Eqs. (1) and (2) with R given by Eqs. (10) and (12), are solved for $n_s(x, t)$ and $n_g(x, t)$ for H and D by means of a stiff ODE integrator. The gas-phase component, $n_g(x, t)$, is, in turn, converted from atomic to molecular composition (as a function of x and t) by Eqs. (16). The time-resolved molecular composition of the gas (in terms of partial pressures) at the output end of the bed is directly compared with the experimental data. The isotopic exchange probability, p, is regarded as a freely varying parameter in the model calculations and is evaluated by fitting the model results to the experimental data.

Initial conditions for the calculations are provided by the experimental values of temperature measured at the start of each experiment, gas pressure (P_{in} and P_{out}), and initial palladium deuteride stoichiometry. The measured value of ϕ and the geometric value for S_o are adjusted for the powder expansion and used in the equations. The gas flow velocity, v_f, which appears in the (one-dimensional) flow terms in Eqs. (2a) and (2b), is the pore velocity in the bed and is calculated from

$$v_f = (K/\mu\phi)\Delta P/\Delta x, \qquad (17)$$

where ΔP is the pressure drop along an axial increment, Δx, of the bed. This expression is obtained from applying the Dupuit–Forchheimer assumption to Darcy's law (*20*). As noted earlier, the gas viscosity changes with the changing gas composition during the exchange process. Using the gas-phase molecular composition at each location and time in the bed, a value of $\mu(x, t)$ for the mixed-species gas is obtained from the Wilke formula (*23*). While values of K, spatially averaged over the bed, are determined from the pressure/flow characteristics of the bed, the calculated gas composition is compared to experimental data obtained at the center of the flow channel (laser beam focal volume). Since potential radial dependences of the flow and exchange process are ignored in the calculations, use of an experimentally measured value of K is questionable. Furthermore, the measured values of K for the hydrided and deuterided beds are observed to be somewhat different. Consequently, K used in Eq. (17) is allowed to vary while the experimental data are fitted. Comparison of the K value obtained from the fit to the measured values shows good agreement and indicates that reasonable accuracy is attained by the one-dimensional flow features of the model. (It is emphasized that the two parameters, p and K, are, to a large extent, uncoupled and each can be varied independently in obtaining a fit to the experimental data.) The molecular mass, M, used to obtain v_t in Eq. (9) is fixed at the value of 3 amu (the simple average molecular mass of the gas).

Several studies of the isotope separation factor, α, for the β-phase H/D/Pd system have been reported, and α is found to be dependent both on temperature and to a lesser degree on the H/D composition ratio. Measurements on palladium black for H/D $\approx$ 1 have yielded room-temperature values of α ranging from about 1.8 to 2.5 (*24–27*). Thermodynamic calculation of α from measurements of the vibrational frequencies of H and D in the lattice gives a value of ~2.3 at room temperature (*18*). While equilibrium values of α are often measured, use of such values in the analysis of dynamical situations, such as the present experiments, may not be justified. A value of $\alpha = 2.4$ from Ref. (*25*) is used to obtain the model results presented in this work (see Results). However, as a consequence of the uncertainties discussed above, the sensitivity of the model results to variations in α is examined (see Discussion). The variation in α due to changes in the H/D ratio of the overall system [~20% (*27*)] is also incorporated in the model.

RESULTS

The data of two exchange experiments (discrete points) are shown in Figs. 2 and 3. These results are representative of the output from a number of runs. The data in Fig. 2 pertain to an experiment in which deuterium was initially sorbed into the Pd powder and hydrogen was flowed through the bed (referred to as a D-to-H exchange),

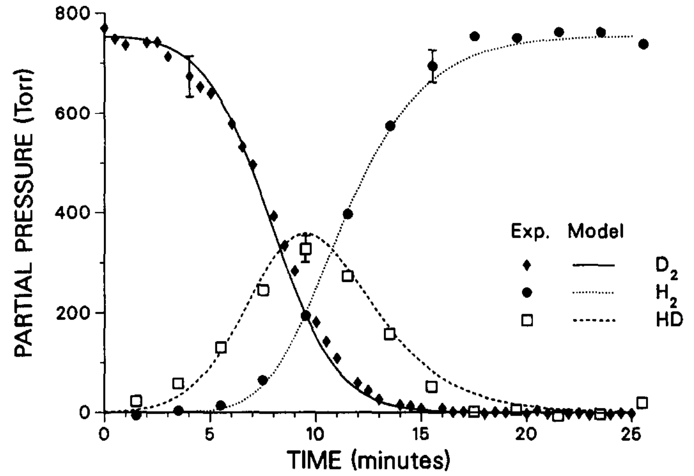

FIG. 2. Composition of gas exiting bed versus time during deuteride-to-hydride (D-to-H) exchange process.

while Fig. 3 depicts the results for the reverse process, an H-to-D exchange reaction, obtained under experimental conditions reasonably similar to those used in the D-to-H exchange run. Note the longer time scale used in Fig. 3. In each case the partial pressures of D_2 and H_2 in the gas exiting from the bed (solid diamonds and circles, respectively) were measured as a function of time during the run, and the partial pressure of HD (open squares) versus time was obtained by subtraction from the measured total output pressure.

For the D-to-H experiment, P_{in} started at 1187 ± 2 torr and monotonically decreased to 1167 ± 2 torr by the end of the run, P_{out} = 753 ± 1 torr throughout the run, Q started at 0.83 ± 0.02 slm and monotonically increased to 0.93 ± 0.02 slm by the end of the run, and the temperature at the start of the experiment was 299 K. For the H-to-D run, P_{in} monotonically in-

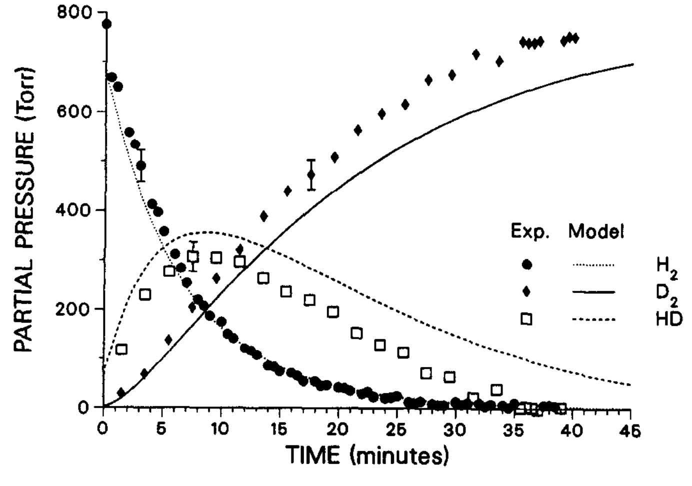

FIG. 3. Composition of gas exiting bed versus time during hydride-to-deuteride (H-to-D) exchange process.

creased from 1124 ± 2 torr at the start of the run to 1128 ± 2 torr at the end, P_{out} = 750 ± 1 torr throughout the run, Q monotonically decreased from 0.71 ± 0.02 slm at the start to 0.66 ± 0.02 slm at the end, and the starting temperature was 299 K. (As mentioned earlier, the variation in P_{in} and Q during the runs is attributed to the change in the composition of the gas flowing through the bed as the exchange process progresses.)

The error bars given on several of the experimental data points indicate the random uncertainty (±2 standard deviations) in the partial pressure determinations and result from a combination of counting statistics errors in the Raman signal (i.e., shot noise), electronics errors, and uncertainties in the total output gas pressure measurement, P_{out}. The error bars given on P_{in} and P_{out} are vendor-specified uncertainties, while the error bars on Q result from the calibration of the mass flow meter against the wet test meter.

Also shown in Figs. 2 and 3 are the results of model calculations (curves) for each experiment. The curves in Fig. 2 for the D-to-H exchange were obtained by fitting the experimental data by using a fixed value of 2.4 for α from Ref. (*25*) and allowing p to vary. The best fit in this case resulted for $p = 2.6 \times 10^{-7}$. Using this value of p, along with $\alpha = 2.4$, the model was then applied to the conditions of the H-to-D experiment and used to predict the output gas composition as a function of time. The results of this prediction are shown in Fig. 3. (The value of K obtained from the model fit of the D-to-H data was used in the model prediction of the H-to-D experiment.)

DISCUSSION

The experimental data shown in Figs. 2 and 3 indicate that there is a significant difference between the D-to-H and H-to-D exchange processes. It can be seen in Fig. 2 that during the initial phase of the D-to-H process, only D_2 is flowing out of the bed. Not until several minutes into the run does hydrogen in the form of HD appear in significant amounts. This result indicates that for the experimental conditions used (powder size, bed length, temperature, for example), the exchange process is efficient enough for the incoming H_2 to be exchanged completely to D_2 before the gas flow exits the bed. (At the gas flow rates involved, the initial amount of overpressure deuterium on the bed is entirely swept past the laser beam in approximately the first 5 to 10 s.) As the exchange process continues past the first few minutes, the input end of the bed becomes depleted in deuterium and some hydrogen passes completely through the bed, first as HD and later as both HD and H_2. This situation is, of course, accompanied by an equivalent decrease in the amount of D_2 exiting from the bed. At still later times, as the deuterium supply in the bed is further exhausted, the D_2 partial pressure decreases toward zero, the production of HD passes through a maximum, and the amount of H_2 increases until in the end it constitutes the entire gas flow.

In the H-to-D exchange (Fig. 3), the time-rates of change of the partial pressures are slower than for the D-to-H exchange, resulting in an overall exchange of the hydride to the deuteride which requires much longer to complete. As indicated by the prompt appearance of HD at the output of the bed, there exists no time interval at the start during which the D_2 gas flowing into the bed is completely exchanged by the time it exits the bed. These features, when coupled with the observation that the conditions of gas pressure and temperature are similar for the two experiments under discussion, indicate that the exchange process is temporally less efficient for the H-to-D conversion than for the D-to-H conversion. The fact that good agreement with the data of both experiments can be obtained from the model using the same value of p (and the temperature measured at the start of each experiment) is significant in that the difference in efficiency between runs is

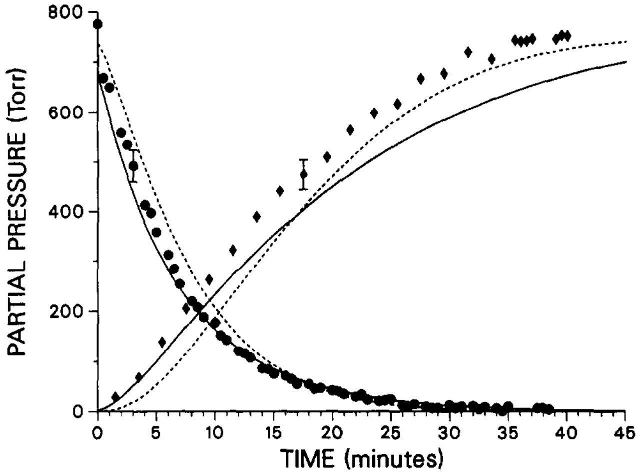

FIG. 4. Comparison of model prediction of output gas composition for the H-to-D exchange process using $p = 2.6 \times 10^{-7}$ and $\alpha = 2.4$ (solid curves) and using $p = 3.7 \times 10^{-7}$ and $\alpha = 1.8$ (dashed curves).

therefore due primarily to the isotope effect. As discussed earlier, this effect, represented by the factor α in the model, favors the D-to-H exchange process while hindering the reverse process.

It is seen from Figs. 2 and 3 that good agreement between the model results and the experimental data can be achieved using an α value (= 2.4) reported in the literature (*25*). In order to ascertain whether or not this agreement can be improved, a model fit to both the D-to-H and the H-to-D exchange data simultaneously was investigated while α as well as p were permitted to vary. It was concluded from this exercise that little improvement in the model results is possible; the curves in Figs. 2 and 3 essentially represent the optimum results. Furthermore, as an indication of the sensitivity of the model results to the use of different values of α, a second fit of the D-to-H data in Fig. 2 using $\alpha = 1.8$ [from Ref. (*24*)] was undertaken. For $p = 3.7 \times 10^{-7}$, this second fit is as good as the one shown in Fig. 2. Using this value of p and 1.8 for α, a second prediction of the H-to-D data in Fig. 3 was made. The results of this calculation are shown (dashed curves) in Fig. 4, along with the previous prediction using $\alpha = 2.4$ and $p = 2.6 \times 10^{-7}$ (solid curves) and the experimental data. For clarity, only the H_2 and D_2 partial pressure results are shown. It is felt that the use of $\alpha = 2.4$ and $p = 2.6 \times 10^{-7}$ yields better agreement with the experimental data.

Several points should be made here concerning the results discussed above. By appropriately varying the values of p and α relative to each other, it is possible to maintain a fit of the D-to-H data of the same quality as shown in Fig. 2 over a range of p and α combinations. On the other hand, the quality of the model prediction for the H-to-D exchange run is not improved over that shown in Fig. 3 when combinations of p and α other than $\alpha = 2.4$ and $p = 2.6 \times 10^{-7}$ are used. In fact, it is not possible even to fit the H-to-D exchange data independently with the same degree of agreement as is obtained in the fit of the D-to-H data shown in Fig. 2. Several reasons have been considered to explain this situation.

Recall that the model results reflect an equilibrium isotopic composition in the gas phase as given by Eqs. (15) and (16). Examination of the experimental data in Figs. 2 and 3 reveals that the composition of the gas exiting from the bed deviates from such an equilibrium mixture to a small degree in the D-to-H exchange and to a more noticeable extent in the H-to-D run. (Such behavior is also exhibited in other exchange data.) This observation raises the possibility that another reaction sequence, different from that given by Eqs. (3), which drives the gas composition away from equilibrium, is, at least, partly operative in this exchange system. Eqs. (3a) and (3b) describe what is called a "single-exchange" process in which only one of the atoms of an incident gas-phase molecule is exchanged with an atom bound to the solid during a gas/surface collision. A "multiple-exchange" process in which both atoms of the incident molecule are exchanged with atoms from the solid has also been studied (*3, 6, 7, 12*). Reactions for this latter process are

$$D_2 + H_s + H_s \rightleftarrows H_2 + D_s + D_s \quad (18a)$$

$$D_2 + H_s + D_s \rightleftarrows HD + D_s + D_s \quad (18b)$$

$$HD + H_s + H_s \rightleftarrows H_2 + H_s + D_s. \quad (18c)$$

In comparison to the single-exchange process, the multiple-exchange mechanism provides an extra reaction path in which a gas-phase H_2 (or D_2) molecule can be formed directly from a D_2 (or H_2) molecule without having to undergo two separate collisions with the surface. Consequently, the multiple-exchange process can lead to HD concentrations which are less than expected from equilibrium. A number of model calculations based on the multiple exchange reactions of Eqs. (18) have been carried out both with and without homophase exchange [Eq. (14)]. In all cases, after optimum fit to the experimental data, such calculations greatly underestimated the amount of HD present in the flow, resulting in poor agreement with experiment and leading to the conclusion that the multiple-exchange process plays, at best, only a small role in the exchange phenomena investigated here.

The inability to fit the H-to-D data as well as is accomplished for the D-to-H data more likely is due to channeling or by-pass gas flow in the H-to-D exchange run which distorts the isotopically equilibrated gas mixture in the bed. Channeled gas flow could occur in the H-to-D exchange as a result of differential powder volume expansion between the palladium hydride and the deuteride. Because of this possibility, agreement between the model results and the experimental data at early times during the H-to-D exchange process is considered more important than at later times.

The experimental conditions of pressure and temperature are chosen such that the powder remains in the β-phase during the isotope exchange process. This constraint is important for several reasons: (a) In the β-phase, the H/Pd and D/Pd stoichiometries at constant temperature and pressure are not greatly different (for the conditions used here, the difference in stoichiometry between the palladium hydride and deuteride is 0.04). As a result, the net amount of gas which is sorbed (desorbed) by the powder over the course of the exchange is small and, thus, the role that this net sorption (desorption) process plays in the overall gas–solid interaction is minimized. As noted earlier, it is assumed in the model that the amount of the isotope leaving the powder equals the amount of the other isotope entering the powder, i.e., constant stoichiometry. (b) By keeping the powder in the β-phase, the change in its volume in going from the hydride to the deuteride or vice versa is expected to be small (*17, 19, 28*) and, therefore, the variation in the bed permeability should be small. This situation is reflected in the model in the use of a constant permeability. (c) The diffusion of hydrogen isotopes in the solid can be quite complex because of the variety of possible situations. Since it is assumed in the model that this solid-state diffusion proceeds rapidly compared to the surface processes and that incorporation of the solid diffusion kinetics into the model is, therefore, not needed, it is important to be aware, as much as possible, of which types of diffusion are taking place in the present experiments, thereby providing definition to the assumption that solid diffusion is fast. In this regard, while the diffusion of hydrogen isotopes in the solid is complicated by the time-varying ternary composition of the powder during the exchange (Pd/H/D), remaining in the β-phase throughout the exchange at least confines the diffusion processes to those which occur in that single phase and avoids diffusion in the α- and/or mixed phase and across phase boundaries.

The temperature reported for each experiment is measured at the start of the run and this value is used in the model calculations. There are, however, several effects which can cause the temperature of the bed to change during the course of the exchange process. Dominant among these is the difference in the heats of adsorption for hydrogen and deuterium in palladium. This difference, about 1 kcal/mol more for hydrogen than for deuterium (*17, 18*), results in local heating in a D-to-H exchange and local cooling in an H-to-D process. Furthermore, the 0.04 difference in stoichiometries between the palladium hydride and the deuteride enhances these heating and cooling effects. A secondary effect as far as magnitude is concerned, which always produces an increase in the powder temperature, stems from the extra amount of gas which is sorbed into the powder due to P_{in} at $t > 0$ being greater than the equilibrium overpressure ($\simeq P_{\text{out}}$) at $t < 0$. Under the experimental conditions used here, the temperature change resulting from these effects is not expected to be large. By assuming that the heat change from the isotope and net sorption processes is confined entirely to the powder (adiabatic approximation), an upper bound on this temperature change of $\Delta T \approx 50°\text{C}$ is obtained. However, the heat capacity of the gas flowing through the bed along with thermal conduction by the gas and the powder to the stainless steel flow channel (which is massive enough to act as a room-temperature heat reservoir in this case) should significantly reduce this adiabatic value.

The impact that the temperature change has on the exchange process is not easy to assess as a consequence of the uncertainty in both the value of the exchange activation energy, E_a, in p, and the magnitude of the temperature variation of α. Nevertheless, it is emphasized that the success of the model in providing a fit to the D-to-H exchange data (in which local heating is expected) and a good prediction of the H-to-D data (local cooling expected), all with the same values of p, α, and temperature (299 K), indicates that the heat change occurring in the bed does not greatly influence the exchange process for the conditions used here.

As stated earlier, the geometric specific surface value of the hydrided (deuterided) powder is used here. In this case, p is interpreted as the isotopic exchange probability averaged over all surface conditions present and the value of p will certainly be material dependent. Alternatively, it would be possible to use an "active-site" specific surface value where only the powder surface area encompassing active sites is included. The isotopic exchange probability, p, would then be a measure of the activity of the "active" sites of the powder surface and would most likely still be a function of the material used.

Independent model fits of data from additional experiments conducted under similar conditions yield values of p which agree to within about a factor of 2. Aside from the effects on p caused by the approximations made in implementing the model, the accuracy of the value of p obtained is, of course, directly related to the accuracy of the values of the various parameters, such as the specific surface, used in the model. The problems involved in connection with this latter issue are somewhat alleviated if only relative values of p are desired.

Comparison of the (material-dependent) values of p obtained in this work with equivalent quantities derived from the results of work previously reported in the literature is complicated by the variety of conditions, methods, and kinetic parameters used and, in some cases, by the lack of experimental detail reported. However, calculation of an isotopic exchange probability from the isotopic exchange rate constants given by Andreev *et al.* (*5, 10*) yields a value of $\sim 10^{-8}$ which, considering the various uncertainties, is in reasonable agreement with the value obtained in this work.

SUMMARY

The macroscopic kinetics of hydrogen–deuterium exchange occurring between the solid and gas phases in gaseous hydrogen (deuterium) flows directed through packed-powder beds of β-phase palladium deuteride (hydride) have been studied in an open gas flow apparatus. The isotopic composition of the gas exiting from the bed has been analyzed as a function of time during the exchange process by spontaneous Raman light scattering. The results of experiments in which the powder is converted from palladium deuteride to palladium hydride (D-to-H exchange) are compared with measurements, under similar pressure/flow conditions, of the reverse process (H-to-D exchange) and a significant difference in the temporal exchange efficiency between the two processes is observed.

A parametric rate equation model which describes the isotope exchange process is presented. The fundamental physical assumption inherent in the model is that the exchange process is rate-limited by the surface interactions. Solution of the model equations under appropriate boundary conditions yields a time history of the process (i.e., hydrogen isotope composition in both the gas and the solid) anywhere in the bed. The model is shown to provide a good description of the experimental data and the computational results indicate that the difference in temporal efficiency observed experimentally can be attributed primarily to the sizable gas-to-solid-phase isotope effect present in the Pd/H/D system. Furthermore, it is found that, for gas-phase atoms colliding with the powder surface, roughly one collision in 10^7 results in isotopic exchange.

ACKNOWLEDGMENTS

The authors thank Prof. W. L. Worrell, J. O. Noell, and M. L. Koszykowski for useful discussions. The technical assistance of F. H. Blair and A. M. Freitas is gratefully acknowledged. The referee's comments regarding the multiple-exchange process are also appreciated. This work is supported by the U.S. Department of Energy.

REFERENCES

1. Sicking, G., *Ber. Bunsen-Ges. Phys. Chem.* **76,** 790 (1972).
2. Sicking, G., Albers, P., and Magomedbekov, E., *J. Less-Common Met.* **89,** 373 (1983).
3. See, for example, Nováková, J., *Catal. Rev.* **4,** 77 (1970).
4. Cheselske, F. J., Wallace, W. E., and Hall, W. K., *J. Phys. Chem.* **63,** 505 (1959); Hall, W. K., Wallace, W. E., and Cheselske, F. J., *J. Phys. Chem.* **65,** 128 (1961).
5. Andreev, B. M., Boreskov, G. K., Chang-tsun, C., and Tsionskii, V. M., *Kinet. Catal.* **7,** 416 (1966).
6. Nováková, J., Jírů, P., and Zavadil, V., *Coll. Czech. Chem. Commun.* **36,** 520 (1971).
7. Nováková, J., Jírů, P., and Zavadil, V., *Coll. Czech. Chem. Commun.* **38,** 2320 (1973).
8. Andreev, B. M., Poleroi, A. S., and Petrenik, O. V., *Sov. At. Energy* **40,** 516 (1976).
9. Andreev, B. M., Perevezentsev, A. N., and Yasenkov, V. I., *Russ. J. Phys. Chem.* **55,** 232 (1981).
10. Andreev, B. M., Perevezentsev, A. N., and Shitikov, V. V., *Russ. J. Phys. Chem.* **55,** 1132 (1981).
11. Tsuchiya, S., Ponec, V., and Sachtler, W. M. H., *J. Catal.* **22,** 280 (1971); Andreev, B. M., Magomedbekov, E. P., and Shitikov, V. V., *Sov. At. Energy* **55,** 535 (1983); Mizuno, N., Katamura, K., Yoneda, Y., and Misono, M., *J. Catal.* **83,** 384 (1983); Andreev, B. M., Magomedbekov, E. P., and Pak, Yu. S., *Russ. J. Phys. Chem.* **58,** 459 (1984); Hodnett, B. K., and Moffat, J. B., *J. Catal.* **91,** 93 (1985).
12. Klier, K., Nováková, J., and Jírů, P., *J. Catal.* **2,** 479 (1963).
13. Palczewska, W., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 24, p. 245. Academic Press, New York, 1975.
14. See, for example, Engel, T., and Ertl, G., *in* "The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis" (D. A. King and D. P. Woodruff, Eds.), Vol. 4, "Fundamental Studies of Heterogeneous Catalysis," p. 195. Elsevier, Amsterdam, 1982.

15. See, for example, Scholten, J. J. F., and Konvalinka, J. A., *J. Catal.* **5,** 1 (1966).
16. Haughey, D. P., and Beveridge, G. S. G., *Canad. J. Chem. Eng.* **47,** 130 (1969).
17. See, for example, Lewis, F. A., "The Palladium Hydrogen System." Academic Press, London, 1967.
18. See, for example, Wicke, E., and Brodowsky, H., *in* "Hydrogen in Metals II" (G. Alefeld and J. Völkl, Eds.), p. 73. Springer-Verlag, Berlin, 1978.
19. See, for example, Peisl, H., *in* "Hydrogen in Metals I" (G. Alefeld and J. Völkl, Eds.), p. 53. Springer-Verlag, Berlin, 1978.
20. Dullien, F. A. L., "Porous Media, Fluid Transport and Pore Structure." Academic Press, New York, 1979.
21. Melius, C. F., and Coronado, P. R., Sandia National Laboratories, unpublished studies.
22. See, for example, Bond, G. C., "Catalysis by Metals." Academic Press, London, 1962.
23. Bird, R. B., Stewart, W. E., and Lightfoot, E. N., "Transport Phenomena." Wiley, New York, 1960; Reid, R. C., Prausnitz, J. M., and Sherwood, T. K., "The Properties of Gases and Liquids." McGraw-Hill, New York, 1977.
24. Glueckauf, E., and Kitt, G. P., *in* "Vapour Phase Chromatography" (D. H. Desty and C. L. A. Harbourn, Eds.), p. 422. Butterworths, London, 1957.
25. Wicke, E., and Nernst, G. H., *Ber. Bunsen-Ges. Phys. Chem.* **68,** 224 (1964).
26. Botter, F., *J. Less-Common Met.* **49,** 111 (1976).
27. Andreev, B. M., Polevoi, A. S., and Perevezentsev, A. N., *Sov. At. Energy* **45,** 710 (1979).
28. Maeland, A., and Flanagan, T. B., *J. Phys. Chem.* **68,** 1419 (1964).