

IV. PHYSICAL ELECTRONICS AND SURFACE PHYSICS*

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A. INFLUENCE OF SURFACE EFFECTS ON THE PERMEATION OF HYDROGEN THROUGH METALS

1. Introduction

The effects of the solution (absorption) of gases in solids and the permeation of gases through solids have proved to be serious problems in the design of various technological devices and processes.¹ As a consequence, there have been numerous studies of the rates of engassing, degassing, and permeation for a variety of gas-solid systems. Although the existing experimental data indicate that the rate-controlling step generally is the diffusion of gas atoms in solids, there is a significant quantity of data indicating that, under certain conditions, the rate-controlling step is a surface process, such as adsorption, penetration, or desorption.

In this report we summarize our current analytical and experimental investigations of the influence of surface processes on the rate of permeation of gases through solids. First, we present a brief description of an analytical model that provides an approximate prediction of the dependence of the permeation rate on the rates of surface processes (adsorption, penetration, and desorption) relative to the rate of the diffusion process. The models of the adsorption and desorption processes include an unknown activation energy which we have attempted to determine experimentally by measuring the spatial distribution of H₂ molecules desorbed from the low-pressure surface of permeation membranes constructed from various materials and subjected to different surface cleaning and/or contamination procedures. Then we report the results of our most recent experiments.

Since it is possible that the existence of an activation energy barrier at a surface may cause the energies of the desorbed molecules to be significantly greater than the thermal-energy level, we have also measured the speed distribution of H₂ desorbed from polycrystalline and single-crystal Ni. These results, which have been reported elsewhere,² are not included in the present report. It is of interest, however, to point

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out that the results indicate that the mean energy of H_2 desorbed from impure Ni surfaces is substantially greater than the thermal-energy level.

2. Analysis

A detailed description of the analysis is now being prepared for publication.³ We shall attempt only to summarize the principal features. The proposed model is based on the potential-energy diagram shown in Fig. IV-1. It is assumed that the gas is a homonuclear diatomic molecule, A_2 , which exists in the atomic state in the adsorbed phase. If the pressure of A_2 in gas phase 1 is higher than in gas phase 2, there will be a net flux (permeation) of molecules from 1 to 2. According to the proposed model, the permeation process includes the following steps.

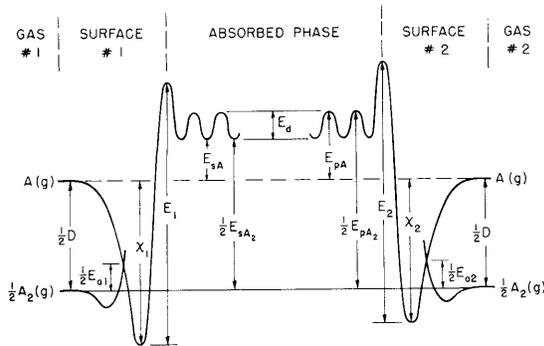


Fig. IV-1. Potential-energy diagram for the interaction of a hypothetical gas, A_2 , with a solid.

Adsorption: Movement of species from gas phase 1 to the adsorbed phase existing on surface 1. It is assumed that the rate of adsorption depends primarily on the magnitude of $1/2 E_{a1}$, the activation energy for dissociative chemisorption [for the reaction $1/2 A_2(g) \rightarrow A(ads)$].

Penetration 1: Movement of species from the adsorbed phase on surface 1 to the absorbed phase just inside this surface; the penetration rate is assumed to depend primarily on E_1 , the activation energy corresponding to $A(ads) \rightarrow A(abs)$.

Diffusion: Movement of species through the solid from a position just inside surface 1 to a position just inside surface 2, with the rate depending primarily on E_d , the activation energy for diffusion of A in the solid. The value of E_d is constant throughout the solid (Fig. IV-1) because we have assumed that the bulk properties of the solid are uniform and that the absorbed phase behaves as an ideal dilute solution.

Penetration 2: Movement of species from the absorbed phase just inside surface 2 to the adsorbed phase on this surface with the rate depending primarily on E_2 . Note that E_1 and E_2 are not shown as equal heights in Fig. IV-1 because we wish to include the possibility of differences that arise from different degrees of contamination of the surfaces.

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Desorption: Movement of species from the adsorbed phase on surface 2 to gas phase 2. Based on detailed balancing arguments, it is assumed that the rate depends on $1/2 E_{a2}$, the activation energy for the reaction $A(\text{ads}) \rightarrow 1/2 A_2(\text{g})$. Note that $1/2 E_{a1}$ and $1/2 E_{a2}$ are not necessarily equal because they may be influenced by the differing states of contamination of the two surfaces.

By assuming simplified models for each of these steps, we have derived approximate expressions for Γ_+ , the "one-way rate" for each step (that is, the rate at which species pass over the particular activation energy barrier in one direction, for example, from left to right in Fig. IV-1). These expressions are explicit functions of the temperature (T), the pressure of A_2 in gas phases 1 and 2 (p_1 and p_2), and the magnitudes of the energies defined in Fig. IV-1. The net rates for each step, J_A , are equal to the difference between the one-way rates for the step in the forward (Γ_+) and backward (Γ_-) directions,

$$J_A = \Gamma_+ - \Gamma_-.$$

Under steady-state conditions, the net rates must be equal in order that all steps satisfy conservation of species A. The magnitudes of the one-way rates may be quite different for the various steps, however, and they depend strongly upon the magnitudes of the activation energies shown in Fig. IV-1. To determine whether the permeation rate is influenced by the rate of a particular step, we define the following parameters:

$$X(\text{ads}) \equiv \Gamma_+(\text{ads})/J_A(\text{diff})$$

$$X(\text{pen}_1) \equiv \Gamma_+(\text{pen}_1)/J_A(\text{diff})$$

$$X(\text{pen}_2) \equiv \Gamma_+(\text{pen}_2)/J_A(\text{diff})$$

$$X(\text{des}) \equiv \Gamma_+(\text{des})/J_A(\text{diff}),$$

where $J_A(\text{diff})$ is the permeation rate corresponding to the limiting case $X \rightarrow \infty$, where the rates of the surface steps are sufficiently large that the diffusion step is the rate-controlling process. That is, $J_A(\text{diff})$ corresponds to the expression generally associated with the permeation rate

$$J_A(\text{diff}) = \frac{P^0}{L} \left(p_1^{1/2} - p_2^{1/2} \right) \exp\left(-\frac{1}{2} E_{pA_2}/RT\right), \quad (1)$$

where P^0 is the preexponential constant of the permeation coefficient, and L is the thickness of the membrane.

Based on the present model, we have derived analytic expressions for J_A in terms of $J_A(\text{diff})$ and X . The results shown in Fig. IV-2 correspond to the special case in which the gas pressure on side 2 is negligible relative to the pressure on side 1. These

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results indicate that the effects of the adsorption and penetration steps are significant only if $X \lesssim 10$, while the effect of the desorption step is significant only if $X \lesssim 10^3$. We

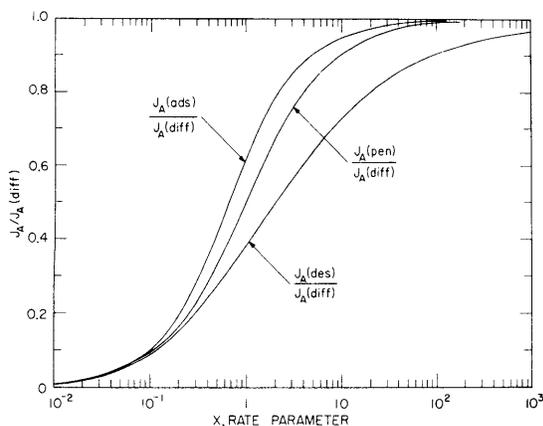


Fig. IV-2.

Theoretical prediction of the effect of surface processes (adsorption, penetration, and desorption) on the rate of permeation of atoms through a solid. J_A is the permeation rate when the effects of surface processes are included, and $J_A(\text{diff})$ is the permeation rate when surface processes are neglected (when diffusion is the rate-controlling process). X is a dimensionless rate parameter.

may use these results either to determine J_A if $J_A(\text{diff})$ and X are known, or to determine X if J_A and $J_A(\text{diff})$ are measured. Since the principal unknown properties that appear in the expressions for X are the activation energies defined in Fig. IV-1, determinations of X from measurements of J_A and $J_A(\text{diff})$ provide an indirect means for determining these energies.

The present analysis provides a semiquantitative explanation of some of the existing experimental data that are inconsistent with the predictions of the permeation equation (Eq. 1) corresponding to the case in which diffusion is the rate-controlling step. Specifically, it accounts for deviations from the linear dependence of J on $p^{1/2}$ and of $\log J$ on $1/T$. These results are now being prepared for publication.³

3. Experiment

a. Introduction

The results of several recent experimental studies^{2, 4-7} demonstrate that the spatial distributions of hydrogen molecules desorbed from various solid surfaces deviate markedly from the previously expected form of diffuse emission; that is, the form $\cos \theta$, where θ is the angle of inspection measured from the surface normal. Instead, the general form of the observed spatial distributions may be described approximately by the empirical form $\cos^d \theta$, where the parameter d , which is determined by fitting this expression to the experimental data, has been reported to be as high as ~ 9 for H_2 desorbed from Ni.^{4, 8} By employing Auger electron spectroscopy, we have demonstrated in a previous study⁷ that d depends strongly upon the chemical composition of the solid surface in the case of H_2 desorbed from Ni. Specifically, we observed that $d \approx 4$ for a

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Ni surface unintentionally contaminated with $\sim 1/2$ monolayer of sulfur, whereas d approached unity as the surface was cleaned by ion bombardment.⁷ We have recently extended this investigation to include other solids (Fe, Pt, Cu, Nb, and stainless steel).

We selected iron as one of the materials to be studied because van Willigen⁴ found that the desorption of H_2 from Fe yields a very sharp (narrow) spatial distribution ($d \approx 6$). The choice of platinum is based on the fact that Smith and Palmer⁶ have observed that $d \approx 3$ for a Pt (111) surface that they believed to be clean. Copper was selected because existing adsorption data^{9,10} indicate that the chemisorption of H_2 on Cu is an activated process. This leads us to hope that the desorption process for this material might result in a spatial distribution that differs from those for other materials. We included niobium and stainless steel because of their technological importance.

b. Apparatus and Procedures

Membrane Assemblies

Since a detailed description of the apparatus has been published,⁷ only a brief summary is given here. The sample is constructed as a thin wall (membrane) at the end of a tube that is connected through a valve to a flask of research grade H_2 . The tube protrudes into an ultrahigh vacuum system, where the end of the tube is heated by a concentric tungsten coil to increase the membrane temperature, thereby increasing the rate of permeation of hydrogen through the membrane. The tube is filled with H_2 at ~ 1 atm pressure, and H atoms diffuse through the heated membrane and recombine on the surface to form molecules that desorb into the evacuated chamber. The spatial distribution of the desorbed molecules is measured by a conventional ionization gauge mounted on a rotatable shaft whose center line is tangential to the membrane surface at its center. The membrane tube assembly is mounted in a manner that enables us to rotate the membrane surface to various working stations,⁷ including an Auger electron spectrometer for determining the surface composition, an ion bombardment gun for surface cleaning, a station for depositing various impurities, and the rotatable ionization gauge for measuring the spatial distribution.

All of the membranes employed in the present study are machined from polycrystalline materials. The Fe and Nb membranes are disks, ~ 0.5 mm thick, cut from rods, 1.27 cm in diameter (Materials Research Corporation, Martz grade). The Pt and stainless-steel membranes are disks cut from sheets (Pt: 0.20 mm sheet from Englehard Industries; stainless steel: 0.25 mm sheet, Type 304). Each of these disks is welded to the end of a stainless-steel cylinder (1.27 cm OD and 0.32 cm ID) which is brazed to a copper tube.

The Cu membrane was formed at the end of a rod, 1.27 cm in diameter (Materials Research, Martz grade) by boring a hole, 0.635 cm in diameter, to obtain the desired membrane thickness, ~ 0.4 mm. This unit is brazed to a stainless-steel tube

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(1.27 cm OD and 0.32 cm ID).

The surfaces of all membranes are mechanically polished, finishing with 0.05 μm alumina. We did not use electrolytic or chemical polishing to remove the worked (deformed) surface layer produced by mechanical polishing, since we had previously found that this did not influence the spatial distributions measured for polycrystalline Ni.

Surface Cleaning Techniques

After installing each membrane and evacuating the system to low pressure ($\sim 10^{-8}$ Torr), the first step was to heat the membrane to an elevated temperature ($\sim 1100^\circ\text{K}$, in most instances) for several hours, thereby degassing the components and stabilizing the structure and composition of the membrane surface. The membrane temperature was then adjusted to the value selected for the measurement of the spatial distribution, and the surface was examined by Auger electron spectroscopy. In all of the present cases the Auger spectra indicated that the heating procedures did not remove all impurities from the surface. The predominant impurities were S, C, and P, and it is generally believed that these occur as the result of bulk impurities that concentrate (segregate) at the surfaces. The procedures that we have used to remove these impurities will now be described.

A satisfactory procedure for removing surface impurities from Fe was to bombard the membrane with argon ions while holding it at the elevated temperature required for measurement of the spatial distribution ($T > 900^\circ\text{K}$). The argon pressure was $\sim 5 \times 10^{-5}$ Torr, and the ion gun was adjusted to provide $\sim 15 \mu\text{A}/\text{cm}^2$ of 250 eV argon ions. Several hours of ion bombardment were required to reduce significantly the impurity concentration on the Fe surface.

The Pt membrane was cleaned both by ion bombardment and by heating the membrane to 1200°K in 10^{-5} Torr of oxygen for several hours.¹¹ This oxidation treatment removed carbon at an appreciable rate only when a tungsten ribbon at $\sim 2400^\circ\text{K}$ was placed directly in front of the membrane. Presumably, the ribbon served as a catalyst for forming atomic oxygen which was effective in reacting with adsorbed C on the membrane surface to form CO and/or CO_2 .

The copper membrane was cleaned by using a similar oxidation treatment for several minutes followed by several hours of annealing at $\sim 1200^\circ\text{K}$. The oxidation treatment removed carbon, and the high-temperature anneal reduced the sulfur on the surface.¹²

Although Nb can be cleaned simply by heating to high temperature,¹³ we could not use this technique because the membrane assembly was not designed to withstand the required temperature. The impurity concentration on the surfaces of both Nb and Type 304 stainless steel was varied by ion bombardment.

c. Experimental Results

Spatial Distributions

The results shown in Fig. IV-3 were obtained after subjecting the membranes to the heating procedure that we have described, but before attempting to clean the surfaces by ion bombardment and/or by oxidation. Therefore, as we shall show, these data represent the spatial distributions of H_2 desorbed from "uncleaned" (impure) surfaces. Notice that the general result is that the spatial distributions for the uncleaned surfaces deviate substantially from the diffuse distribution ($\cos \theta$), and they may be described approximately by the form $\cos^d \theta$, where d ranges from ~ 2.5 for Nb to ~ 7 for Fe.

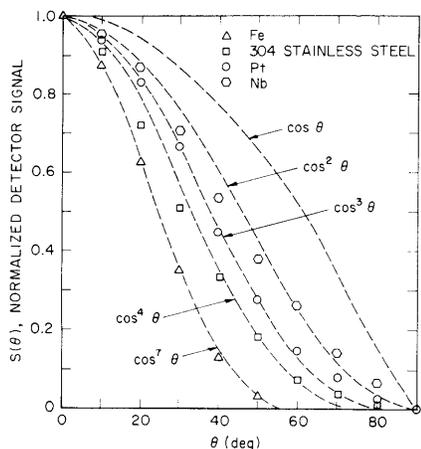


Fig. IV-3.

Spatial distributions of H_2 desorbed from uncleaned (impure) surfaces of polycrystalline Fe, Pt, Nb, and Type 304 stainless-steel samples. Temperatures: Fe = 1140°K; Pt = 1225°K; 304 SS = 1180°K; Nb = 850°K. Dashed curves represent the form of the empirical expression, $\cos^d \theta$, for various values of d .

The present result of $d \approx 7$ for contaminated Fe agrees quite closely with van Willigen's data⁴ which indicate that $d \approx 6$. The Auger spectrum recorded for this surface (before any attempt to clean by ion bombardment) exhibited only Fe and S peaks with the value of I_S/I_{Fe} , the ratio of the Auger peaks for S at 150 V and for Fe at 48 V being ~ 0.3 . After brief ion bombardment at 1200°K, phosphorus appeared in the Auger spectrum in addition to Fe and S, and the spatial distribution broadened to the extent that d decreased to ~ 4 . After several hours of ion bombardment, I_S/I_{Fe} was reduced to 0.04 and I_P/I_{Fe} to 0.08, while d decreased to ~ 3 . Attempts to deposit pure layers of either S or C on Fe were unsuccessful, as these elements appeared to diffuse into the bulk almost as fast as they could be deposited. Deposition of S did increase I_S/I_{Fe} to ~ 2.6 , with the corresponding spatial distribution characterized by $d \approx 2.5$.

The present value of $d \approx 3$ for uncleaned Pt (Fig. IV-3) is identical to the result obtained by Smith and Palmer⁶ for desorption of HD from a Pt (111) crystal. On the basis of indirect evidence, Smith and Palmer suggest that their Pt surface was clean. In our case, however, the Auger spectrum of the uncleaned Pt sample shows that C and

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P are present as surface impurities. This sample was then subjected to extended ion bombardment and oxidation processes, with the result that the Auger peak corresponding to C was reduced to $\sim 10\%$ of its initial value. Since this partial cleaning process resulted in a broadening of the spatial distribution to $d \approx 1.8$, we suspect that a completely clean Pt surface would have a diffuse distribution ($d = 1$), which is identical to the trend we have observed previously in Ni.⁷ On the basis of these limited data, we suggest that the nondiffuse spatial distributions observed by Smith⁶ and Palmer⁵ for both Pt and Ni are the result of partial contamination of the crystal surfaces.

The spatial distribution for uncleaned Nb is characterized by $d \approx 2.5$ (Fig. IV-3), and the principal surface impurities detected by Auger spectroscopy are S and C. Although we did not succeed in attaining a completely clean Nb surface even after prolonged ion bombardment, we did observe that the distribution broadened when the surface was partially cleaned.

As seen in Fig. IV-3, d is roughly 4.5 for uncleaned stainless steel. The Auger spectrum for this surface exhibited peaks corresponding to Fe, Cr, Ni, and S. Ion bombardment of the sample resulted in a decrease in the peak corresponding to S and a broadening of the spatial distribution.

Copper was studied in greater detail because the results for Cu deviated from the general trend observed for the other materials that we have considered. The spatial distribution measured for the uncleaned Cu surface is presented in Fig. IV-4 (data designated as "uncleaned Cu"), and we see that $d \approx 6$. The corresponding Auger spectrum is shown in Fig. IV-5a, and the principal impurities are observed to be C and O. Although the distribution broadened slightly as the surface was cleaned by ion bombardment, it did not tend toward a diffuse distribution in the limit of a completely clean surface. Instead, the limiting distribution appeared to be characterized by $d \approx 4$, as illustrated in Fig. IV-4 by the data designated as "clean Cu." The Auger spectrum corresponding to this surface condition is shown in Fig. IV-5b, and we see that both C and O have been reduced below the limit of detection, and the only impurity observed is a very small peak at ~ 140 V which probably corresponds to S. Similar results were obtained with a second Cu sample.

After obtaining these results, we attempted to determine whether the spatial distribution would become diffuse when a layer of carbon is deposited on the Cu surface. This test was motivated by our previous results⁷ which show that a diffuse distribution results when a layer of C is deposited on Ni. The Auger spectrum for this surface indicated that enough C had been deposited to eliminate detection of the Cu substrate. As shown by the data in Fig. IV-4, the spatial distribution was essentially diffuse for the C-covered Cu surface. Subsequently, the carbon was removed by oxidation and the spatial distribution was observed to return to the form characterized by $d \approx 4$, while the Auger spectrum returned essentially to the previous recording (Fig. IV-5b).

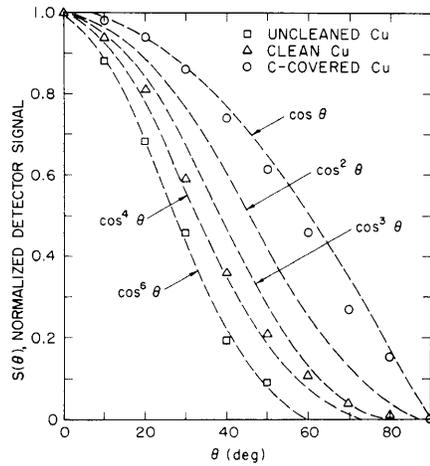


Fig. IV-4. Spatial distributions of H_2 desorbed from a polycrystalline Cu sample for three different conditions of the surface.

- uncleaned surface at 1245°K. The corresponding Auger spectrum (Fig. IV-5a) indicates that C and O are the principal surface impurities.
- △ clean surface 1225°K. The corresponding Auger spectrum (Fig. IV-5b) indicates that the surface is clean except for a trace of S.
- carbon surface layer deposited on the Cu sample at 1125°K.

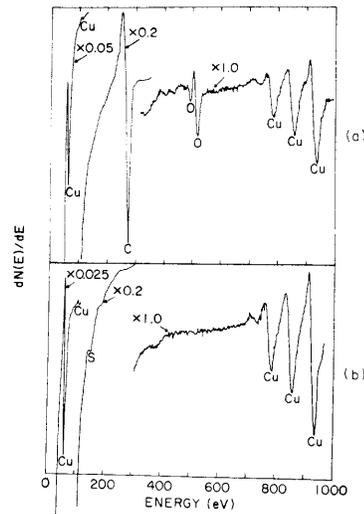


Fig. IV-5. Auger spectra of the Cu sample (a) before and (b) after cleaning the surface. Temperature: $\sim 1200^\circ\text{K}$. Electron beam: $150 \mu\text{A}$ at 2700 V.

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It was generally observed for all of the materials considered in this study that the spatial distributions did not vary significantly with the temperature of the sample, except in a few cases when the temperature change produced a significant change in the concentrations of surface impurities. The temperature range was rather limited, however, because the permeation rate (and therefore the detector signal) decreases sharply as the temperature is reduced.

Permeation Rates

Since the shape of the spatial distribution for a particular material does not vary significantly with temperature, the detector signal $S(\theta)$ at any given value of θ should be directly proportional to the rate of permeation of hydrogen through the material. Therefore, if the conditions are such that the permeation rate is limited by the diffusion of atoms through the bulk rather than by surface processes,³ we would expect, for the data obtained for a particular material, that an Arrhenius plot of $\log S(\theta)$ against $10^3/T$ would yield a straight line of slope equal to $-Q/R$, where Q is the apparent activation energy for permeation of hydrogen through the material, and R is the universal gas constant. [Existing permeation data are reported in terms of either Q or E_p , where $E_p = 2Q$ represents the energy associated with raising two atoms from the gas phase

(where they exist as an H_2 molecule) to the level of the permeation barrier in the solid.] By comparing the resulting values of Q with published values based on conventional permeation techniques, we may determine whether our data are reasonable or whether there is an indication that the permeation rate is influenced by surface processes that may depend on the concentration of surface impurities on the low-pressure side of the membrane.

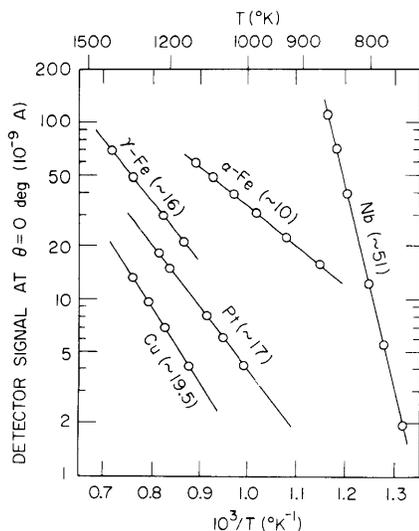


Fig. IV-6.

Temperature dependence of the rate of permeation of hydrogen through Fe, Pt, Cu, and Nb. The values in parenthesis are the apparent activation energies, Q (kcal/mole of H atoms), calculated from the slopes of the lines through data points.

Our data for Fe, Pt, Nb, and Cu are presented in Fig. IV-6, and we see that the results for these materials may be represented by straight lines. Our data for Ni have been reported previously.² The data for stainless steel are omitted because the spatial distribution varied with temperature as a result of the dependence of the surface

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composition on temperature. The apparent activation energy for permeation, Q , was determined from the slope of the line for each material, and the results are in parenthesis in Fig. IV-6.

Iron offers a particularly interesting case because at 1183°K it undergoes an allotropic transformation from body-centered cubic (α -Fe) to face-centered cubic (γ -Fe). The data in Fig. IV-6 show that this change in crystal structure produces a marked change in the permeation rate, as has been reported by other investigators using more conventional permeation measurement techniques.¹⁴ We observed: (i) the results were essentially reversible (that is, the data were approximately the same for both increasing and decreasing temperature); (ii) the concentration of the principal surface impurity, sulfur, did not change when the transformation occurred ($I_S/I_{Fe} \approx 0.3$); (iii) although the magnitude of the spatial distribution was affected significantly by the transformation, the form of the distribution appeared to be constant ($d \approx 7$); (iv) the observed temperature of the transformation was $\sim 50^\circ$ lower than the accepted value (1183°K), probably because of inaccuracies associated with our temperature measurements. The value of Q for α -Fe (~ 10 kcal/mole) is in good agreement with the average of the data tabulated by Barrer¹⁵ (9.7 kcal/mole), whereas the value for γ -Fe (~ 16 kcal/mole) is slightly below ($\sim 15\%$) the results of Post and Ham.¹⁴

The values of Q for Pt (~ 17 kcal/mole) and for Cu (~ 19.5 kcal/mole) differ $\sim 11\%$ from the averages of the data tabulated by Barrer¹⁵ (19.1 and 17.7 kcal/mole for Pt and Cu, respectively).

According to existing solubility data,¹⁶ the H-Nb system does not behave as an ideal dilute solution under the conditions of the present experiment ($p \approx 1$ atm, $T \approx 750^\circ\text{K}$ to 850°K). In fact, the concentration of H in Nb is sufficiently high under these conditions to suggest that Q , the apparent activation energy for permeation, will vary with pressure and temperature; therefore, we would not expect our data for Nb to appear as a straight line in Fig. IV-6. Although the data do appear to fall on a straight line corresponding to $Q \approx 51$ kcal/mole, we suspect that deviations would be observed if the temperature range were increased. (The present range is extremely small, ~ 750 - 850°K). These data agree qualitatively with experimental data obtained by Steigerwald¹⁷ at slightly lower temperatures. Since the apparent activation energies of our data and of Steigerwald's data are substantially higher than the values observed at higher temperatures,¹⁸ it is possible that surface effects are influential. We plan to examine this possibility in future studies.

4. Conclusion

The results of our experiments indicate that the desorption process of hydrogen from various materials is influenced by surface impurities to the degree that substantial changes in the spatial distribution of the desorbed molecules are observed when the

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impurities are varied. On the other hand, except possibly for H-Nb, the permeation measurements indicate that the desorption process is not influenced to the degree that detectable changes in the permeation rates are observed when the impurities and temperatures are varied. On the basis of the analysis described here, it is rather unlikely that the desorption process will be the rate-controlling step under the conditions of the present experiments. We plan to perform more tests at lower temperatures and pressures at which surface processes should be more significant.

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References

1. For example, see J. D. Fast, Interactions of Metals and Gases, Vol. 1 (Academic Press, Inc., New York, 1965).
2. A. E. Dabiri, T. J. Lee, and R. E. Stickney, Surface Sci. 26, 522 (1971).
3. R. E. Stickney, R. L. Levin, and D. L. Shupe "Analysis of the Influence of Surface Processes on the Rate of Permeation of Gases through Solids" (in preparation).
4. W. van Willigen, Phys. Letters 28A, 80 (1968).
5. R. L. Palmer, J. N. Smith, Jr., H. Saltzburg, and D. R. O'Keefe, J. Chem. Phys. 53, 1666 (1970).
6. J. N. Smith, Jr., and R. L. Palmer, J. Chem. Phys. (in press).
7. T. L. Bradley, A. E. Dabiri, and R. E. Stickney, Surface Sci. 29, 590 (1972).
8. Van Willigen has informed us privately that he has not been able to reproduce his initial results⁴ that indicated $d \approx 9$ for H₂ desorbed from polycrystalline Ni; instead, his subsequent data indicate $d \approx 4$.
9. For example, see D. O. Hayward and B. M. W. Trapnell, Chemisorption (Butterworths Scientific Publications, London, 1964), p. 75.
10. C. S. Alexander and J. Pritchard, Trans. Faraday Soc. (in press).
11. P. W. Palmberg, in G. A. Somorjai (Ed.), The Structure and Chemistry of Solid Surfaces (John Wiley and Sons, Inc., New York, 1969), p. 29.
12. L. H. Jenkins and M. F. Chung, Surface Sci. 24, 125 (1971).
13. T. W. Haas, J. T. Grant, and G. J. Dooley III, J. Vac. Sci. Technol. 7, 43 (1970).
14. C. B. Post and W. R. Ham, J. Chem. Phys. 5, 915 (1937); P. L. Chang and W. D. G. Bennett, J. Iron and Steel Inst. 170, 205 (1952).
15. R. Barrer, Diffusion In and Through Solids (Cambridge University Press, London, 1951), p. 168.
16. A. D. McQuillan and A. D. Wallbank, J. Chem. Phys. 52, 965 (1970); E. Veleckis and R. H. Edwards, J. Phys. Chem. 73, 683 (1969); W. M. Albrecht, W. D. Goode, and M. W. Mallett, J. Electrochem. Soc. 106, 981 (1959).
17. E. A. Steigerwald, "The Permeation of Hydrogen through Materials for the Sunflower System," NASA CR-54004, NASA ER-5623, November 1963.
18. D. W. Rudd, D. W. Vose, and S. Johnson, J. Phys. Chem. 66, 351 (1962).