

## II. PHYSICAL ELECTRONICS AND SURFACE PHYSICS

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#### A. PERMEATION OF HYDROGEN THROUGH METALS

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The absorption and permeation of hydrogen in metals occurs in a variety of technological processes and systems, and in some cases the results are extremely detrimental (e.g., hydrogen embrittlement, stress corrosion, degradation of electrical and magnetic properties, undesired loss (or gain) of hydrogen, etc.). In an increasing number of applications the hydrogen pressure,  $p$ , is extremely low, falling considerably below the range of existing permeation data.<sup>1</sup> In these cases it is usually assumed that the permeation rate,  $J$ , may be estimated by extrapolation of experimental data obtained at higher pressures. As pointed out elsewhere,<sup>1</sup> the common extrapolation based on the relation  $J \propto p^{1/2}$  is not valid at extremely low pressures because there are various gas phase and surface processes that become increasingly important with decreasing pressure. Consequently, the present practice of estimating permeation rates by the common extrapolation method may lead to serious errors.

This report summarizes our attempts to provide more reliable data on the permeation of hydrogen through various materials. We shall concentrate on our current theoretical investigation of permeation at low pressures and present our most recent experimental results concerning the permeation of hydrogen through niobium. The results of our earlier investigations have been described in previous publications.<sup>2-6</sup>

##### 1. Low-Pressure Permeation

The exceptionally high permeability of some metals (e.g., Nb, V, and Pd) results in an important constraint on extrapolating available permeation data to very low pressures. This constraint arises from the requirement of conservation of hydrogen on the high-pressure side of the metal, which can be stated as

$$J_{H_2} \leq \Gamma_{1H_2} + \frac{1}{2} \Gamma_{1H} \quad (1)$$

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where  $J_{H_2}$  is the hydrogen permeation rate (for convenience expressed in terms of molecules rather than atoms), and  $\Gamma_{1H_2}$  and  $\Gamma_{1H}$  are the rates at which gas molecules and atoms adsorb on the high-pressure side of the metal. If we consider only the conditions where the degree of dissociation of the gas is extremely small, then

$$p_{1H}/p_{1H_2} \ll 1 \quad \text{and} \quad \frac{1}{2} \Gamma_{1H}/\Gamma_{1H_2} \ll 1.$$

Consequently, for simple diffusion-limited permeation through a membrane of permeability  $P_{H_2}$  and thickness  $L$ ,  $J_{H_2}$  varies as the square root of pressure<sup>7</sup>

$$J_{H_2}(\text{diff}) = P_{H_2} (p_1^{1/2} - p_2^{1/2})/L, \quad (2)$$

where  $p_1$  and  $p_2$  are the hydrogen pressures at the upstream and downstream surfaces of the membrane. But according to simple kinetic theory,  $\Gamma_{1H_2}$  is a linear function of pressure. As a result,  $\Gamma_{1H_2}$  will decrease more rapidly than  $J_{H_2}(\text{diff})$  as the pressure is decreased, and there will be a limiting pressure below which this constraint cannot be satisfied. This limiting pressure represents the situation in which the adsorption rate is no longer sufficiently large relative to the diffusion rate to establish local equilibrium between gaseous and adsorbed hydrogen at the high-pressure surface; that is, the equilibrium relation  $x = Sp^{1/2}$ , where  $x$  is the atom fraction of hydrogen and  $S$  is the solubility, will not be valid, and therefore the conventional diffusion-limited permeation equation becomes inadequate at pressures that are several orders of magnitude above the limiting pressure.

If we assume that the permeation process is adsorption-rate limited; that is, local equilibrium no longer exists between the gas phase and the adlayer (the hydrogen adsorbed on the metal surface), then an expression for  $J_{H_2}$  can be derived if the following conditions are satisfied.<sup>3</sup>

1. The gas phase remains in local equilibrium so that the adsorption rates are given by

$$\begin{aligned} \Gamma_{1H} &= \zeta_H p_{1H} (2\pi m_H kT)^{-1/2} \\ \Gamma_{1H_2} &= \zeta_{H_2} p_{1H_2} (2\pi m_{H_2} kT)^{-1/2}, \end{aligned} \quad (3)$$

where  $\zeta_H$  and  $\zeta_{H_2}$  are the equilibration probabilities for H and  $H_2$ , respectively. [Note:  $\zeta$  is defined as the probability that the collision of a particle with the solid

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surface will lead to adsorption and complete equilibration rather than reflection.]

2. The adlayer remains in local equilibrium so that its state may be described in terms of  $T$ ,  $p_{1H}^*$  and  $p_{1H_2}^*$ , where the stars indicate that the partial pressures are the hypothetical values that would exist for the same temperature and adlayer concentration if there were equilibrium between the gas and the adlayer. Therefore, the principle of detailed balancing enables us to express the desorption rates as

$$R_{1H}^* = \zeta_H p_{1H}^* (2\pi m_H kT)^{-1/2}$$

$$R_{1H_2}^* = \zeta_{H_2} p_{1H_2}^* (2\pi m_{H_2} kT)^{-1/2}. \quad (4)$$

3. Local equilibrium exists between the adlayer and ablayer (the hydrogen absorbed in the metal just below the surface), which allows us to write an expression for the adsorption-limited permeation rate through a membrane:

$$J_{H_2}(\text{ads}) = P_{H_2} \left( p_{1H_2}^{*1/2} - p_{2H_2}^{*1/2} \right) / L. \quad (5)$$

Now the fluxes of molecules in and out of the adlayer must satisfy the following steady-state conservation relation

$$\Gamma_{1H_2} + \frac{1}{2} \Gamma_{1H} = R_{1H_2}^* + \frac{1}{2} R_{1H}^* + J_{H_2}(\text{ads}). \quad (6)$$

Consequently, by combining Eqs. 3-6 under the assumptions that the pressure on the downstream side of the membrane is negligible with respect to that on the upstream side ( $p_2/p_1 \ll 1$ ) and that equilibrium conditions exist in the high-pressure gas phase ( $p_{1H}/p_{1H_2}^{1/2} = K_p$ , where  $p_{1H} + p_{1H_2} = p_1$ ), the following expression for  $J_{H_2}(\text{ads})$  can be derived.<sup>3</sup>

$$\frac{J_{H_2}(\text{ads})}{J_{H_2}(\text{diff})} = \frac{1}{2} \lambda_{\text{ads}} \left\{ \left[ 1 + 4 \frac{\gamma_{\text{ads}}}{\lambda_{\text{ads}}^2} \right]^{1/2} - 1 \right\}, \quad (7)$$

where

$$\lambda_{\text{ads}} = \frac{K_p^2}{\sqrt{2} p_{1H}} \left( \frac{\zeta_H}{\zeta_{H_2}} \right) + \frac{K_p (P_{H_2}/L)}{p_{1H} \zeta_{H_2} (2\pi m_{H_2} kT)^{-1/2}} \quad (8)$$

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$$\gamma_{\text{ads}} = 1 + \frac{K_p^2}{\sqrt{2} p_{1H}} \left( \frac{\zeta_H}{\zeta_{H_2}} \right) \quad (9)$$

$$J_{H_2}(\text{diff}) = \frac{P_{H_2}}{L} \left( \frac{p_{1H}}{K_p} \right) \quad (10)$$

$$p_{1H} = \frac{1}{2} K_p^2 \left\{ \left[ 1 + \frac{4p_1}{K_p^2} \right]^{1/2} - 1 \right\}. \quad (11)$$

The present analysis provides a semiquantitative explanation of some of the existing experimental data that are inconsistent with the predictions of the diffusion-limited permeation equation (Eq. 2). Specifically, it accounts for deviations<sup>3, 5</sup> from the linear dependence of  $J_{H_2}$  on  $p_1^{1/2}$  and of  $\log J_{H_2}$  on  $1/T$ .

Since our present purpose is to determine the effect of low pressures on the

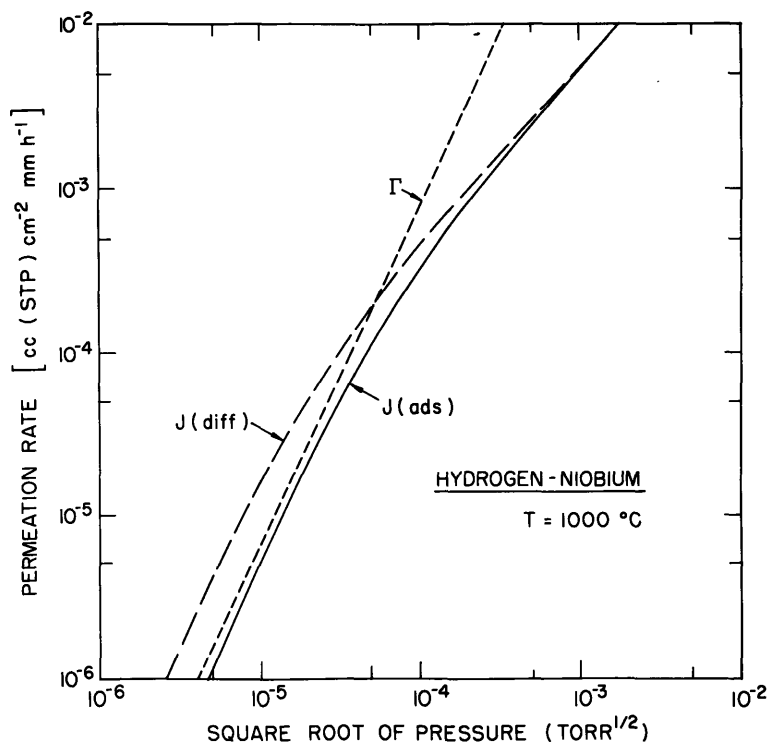


Fig. II-1. Theoretical prediction of the pressure dependence of the adsorption rate  $[\Gamma]$ , the diffusion-limited permeation rate  $[J(\text{diff})]$ , and the adsorption-limited permeation rate  $[J(\text{ads})]$  for a hydrogen-niobium system at a temperature of  $1000^\circ \text{C}$ .

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permeation rate, it suffices that we discuss only the dependence of  $J_{H_2}$  on  $p_1$ . Equations 3, 7, and 10 are plotted in Fig. II-1 as a function of the square root of the total pressure ( $p_1^{1/2}$ ) for the case of niobium at a temperature of 1000°C. In plotting these equations we have assumed: (i)  $\zeta_{1H} = \zeta_{1H_2} = 1$ ; (ii) an equilibrium degree of dissociation of hydrogen exists in gas phase 1; and (iii) the permeability constant of hydrogen in niobium is the "best value" suggested by Stickney.<sup>1</sup> It can be seen that, although  $J(\text{diff})$  becomes greater than  $\Gamma$  in the low-pressure limit, the adsorption-limited permeation rate nowhere exceeds either the adsorption rate or the diffusion-limited permeation rate, but approaches these limits for low and high pressures.

A useful number to refer to when considering surface-limited permeation is the pressure below which the inequality of Eq. 1 is violated when  $J_{H_2}$  is incorrectly assumed to be the diffusion-limited permeation rate (Eq. 2). By using Eqs. 1, 3, and 10, it can be shown that this pressure, which we shall call the "critical pressure," is nonzero if and only if

$$\frac{P_{H_2}/L}{(2\pi m_{H_2} kT)^{-1/2}} > \frac{K_p}{\sqrt{2}} \quad (12)$$

when we assume  $\zeta_H = \zeta_{H_2} = 1$ . This inequality is satisfied for the cases of 1-mm thick niobium and vanadium membranes at 1000°C when

$$\text{Niobium: } p_{1)\text{crit}} \sim 2 \times 10^{-9} \text{ Torr}$$

$$\text{Vanadium: } p_{1)\text{crit}} \sim 6 \times 10^{-7} \text{ Torr.}$$

It is not satisfied for most other metals under the same conditions, however, since the permeation rate generally is so low that it will always be less than the hydrogen arrival rate at surface 1.

The critical pressure for niobium at 1000°C is so low that it would be extremely difficult to perform a convincing experimental verification. Since vanadium's critical pressure is higher by two orders of magnitude, we are now planning an experimental study of this material at very low pressures with temperatures in the 800-1200°C range.

### 2. Experiment

#### a. Introductory Remarks

Experimental data on the permeation of hydrogen through niobium are extremely sparse and of questionable reliability.<sup>1</sup> The temperature ranges covered by Steigerwald<sup>8</sup>

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(215-490°C) and Rudd, Vose, and Johnson<sup>9</sup> (950-1065°C) are very narrow and do not overlap. Furthermore, their data cover an extremely limited range of pressure, since the driving pressure used by Steigerwald<sup>8</sup> was held constant at 1 atm while Rudd et al.<sup>9</sup> conducted their experiments at 1.1, 1.5, and 2.0 atm. For the pressure and temperature conditions of these studies, the hydrogen concentrations in the ablayer near the upstream surfaces were sufficiently high that the H-Nb system should not behave as an ideal dilute solution. Specifically, on the basis of the solubility data of Veleckis and Edwards,<sup>10</sup> we find that the concentrations in both instances were greater than ~2 at. %, which is around an order of magnitude above the level where the behavior of the system begins to deviate significantly from an ideal dilute solution. As a result, it is not valid to extrapolate the existing data<sup>8,9</sup> to low pressures by using the common permeation equation (Eq. 2) which is based on the premise that the solution is ideally dilute (i.e., that Sievert's law applies,  $x = Sp^{1/2}$ ). Consequently, it was the purpose of this investigation to gather steady-state permeation data over the widest possible pressure and temperature ranges that our apparatus would permit, including regions where the H-Nb system behaves as an ideal dilute solution.

### b. Experimental Apparatus and Procedures

The experimental apparatus used in this study is shown in Fig. II-2. It includes two ultrahigh vacuum systems connected by flexible stainless-steel bellows: an input system (System II) used for the introduction of hydrogen into the specimen, and an output system (System I) for analysis and removal of the permeated hydrogen.

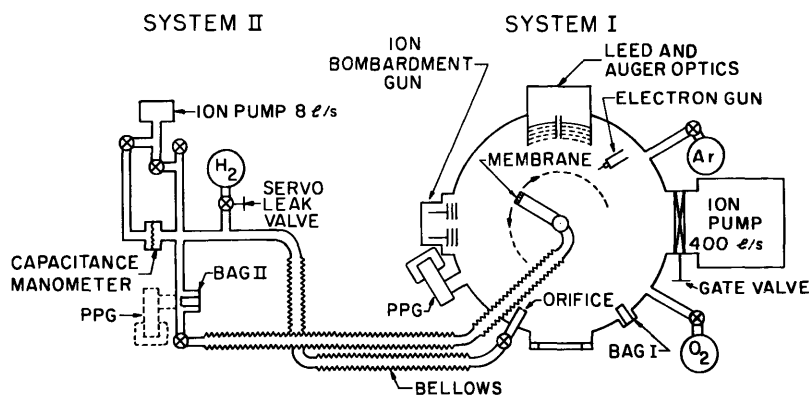


Fig. II-2. Experimental apparatus for measuring the permeation rate of gases through metals.

The sample is constructed as a thin wall (membrane) at the end of a tube which is connected to System II in which selected driving pressures can be constantly maintained by an automatic pressure controller in conjunction with either an ionization gage (BAG-II)

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or a capacitance manometer. The membrane assembly is a polycrystalline niobium disk 0.76 mm (0.030 in) thick, 1.27 cm (0.50 in) diameter, cut from a piece of niobium foil 0.76 mm (0.030 in) thick (Materials Research Corporation, Marz Grade). The disk is electron-beam welded to the end of a thin wall (0.38 mm thick), 1.27 cm ID, low-porosity, vapor-deposited tungsten tube which is brazed into a stainless-steel flange. The assembly is mounted inside System I in a manner that enables us to rotate it to various working stations which include an ion bombardment gun and an Auger electron spectrometer.<sup>4</sup> The membrane end of the tube is heated by a concentric tungsten coil, and the membrane temperature is monitored by a Pt-Pt-10% Rh thermocouple spot-welded onto the membrane at the e-beam weld. The entire assembly was observed to be impermeable to helium at all experimental temperatures, thereby indicating that the assembly was free from leaks that could confuse the permeation data for hydrogen.

Both ionization gages, BAG-I and BAG-II, employed thoria-coated filaments operated at 100  $\mu$ A ionizing current, while the partial pressure mass spectrometer (PPG) employed a tungsten filament at 1 mA. The BAG sensitivities, based on the calibration of nominally identical gages against the capacitance manometer, were taken to be  $3.85 \pm .05 \text{ Torr}^{-1}$  for hydrogen. The PPG was calibrated against BAG-I and was found to have a hydrogen sensitivity of  $2.19 \pm .05 \text{ Torr}^{-1}$ . During permeation, the hydrogen pressure in System I was monitored by the PPG and BAG-I and it ranged between  $1 \times 10^{-9} \text{ Torr}$  and  $6 \times 10^{-6} \text{ Torr}$ , depending upon the membrane temperature and the driving pressure. System II was operated as a static system for driving pressures above  $3 \times 10^{-3} \text{ Torr}$  and as a steady flow system for pressures below  $1 \times 10^{-3} \text{ Torr}$ . Hydrogen admitted to System II was Airco research grade (99.9995%).

The single niobium membrane used in this investigation was not mechanically polished, but the entire membrane assembly was degreased by rinsing in trichlorethylene and acetone. Initially, the membrane was outgassed at 1500°K for 18 hours while both vacuum systems were baked out to attain a pressure in the  $10^{-9} \text{ Torr}$  range. The permeation measurements were conducted for membrane temperatures in the range 588-1250°K and hydrogen pressures in the range  $1.0 \times 10^{-4} \text{ Torr}$ -10.24 Torr. We have not attempted to clean the membrane surface by chemical reaction with gaseous oxygen or by ion bombardment, nor have we used the Auger spectrometer to determine the chemical composition of the downstream surface.

### c. Results

The steady-state influx of hydrogen through the membrane into System I can be equated to the throughput of hydrogen,

$$J \cdot A = (p_{\text{H}_2} - p_{\text{H}_2}^0) S_{\text{H}_2},$$

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where  $p_{\text{H}_2}$  is the measured partial pressure of  $\text{H}_2$  in System I,  $p_{\text{H}_2}^{\text{o}}$  is the residual  $\text{H}_2$  partial pressure in System I with no permeation taking place but with the membrane at the operating temperature,  $S_{\text{H}_2}$  is the measured pumping speed for  $\text{H}_2$  provided by a partially valved-off ion pump,  $J$  is the  $\text{H}_2$  permeation rate, and  $A$  is the surface area of the membrane. This equation assumes that the permeation of hydrogen through niobium is the only source of  $\text{H}_2$  and that the ion pump is the only significant mechanism for removing  $\text{H}_2$ . We found that this assumption becomes invalid at very low pressures and temperatures, and this placed a lower limit on our experimental range.

The pumping speed of the partially valved-off ion pump was calibrated by use of a standard known conductance technique<sup>11</sup> and was found to be  $60.7 \pm 4.5$  l/s of hydrogen over the pressure range  $1 \times 10^{-8}$  Torr- $1 \times 10^{-5}$  Torr. The pumping speed was found to be essentially independent of membrane temperature, although  $p_{\text{H}_2}^{\text{o}}$  depended somewhat on history and strongly on sample temperature.

We estimate that the variation in membrane temperature was of the order of  $\pm 10^\circ\text{C}$ . This is based on two facts: (i) the power required to heat the membrane to a given temperature was essentially constant, independent of history and of the hydrogen driving pressure; and (ii) for a limited time a Ch-Al thermocouple, in addition to a Pt-Pt 10% Rh thermocouple, was used to monitor the membrane temperature and the difference in temperature readings was less than  $15^\circ\text{C}$ . On the basis of available data,<sup>1</sup> we also estimate that the rate of permeation of hydrogen through the hot portion of the thin-wall tungsten tube is negligible relative to the permeation of hydrogen through the niobium membrane.

Typical steady-state permeation data are plotted in Figs. II-3 and II-4. As can be seen in Fig. II-3, the permeation rate exhibits the expected  $p^{1/2}$  dependence at low pressures and high temperatures; however, at higher pressures and lower temperatures the data indicate that the permeation rate becomes approximately linearly dependent on the pressure. Also, from Fig. II-4 it can be seen that the slope of  $\log J$  vs  $1/T$  is not constant but varies between two extremes:

1. For higher temperatures ( $T \gtrsim 800^\circ\text{K}$ ),

$$\frac{d \log_e J}{d(10^3/T)} \sim -5.0^\circ\text{K}$$

2. For lower temperatures ( $T \lesssim 800^\circ\text{K}$ ),

$$\frac{d \log_e J}{d(10^3/T)} \sim -7.7^\circ\text{K}$$

### d. Discussion

On the basis of Figs. II-3 and II-4, we must conclude that the steady-state permeation



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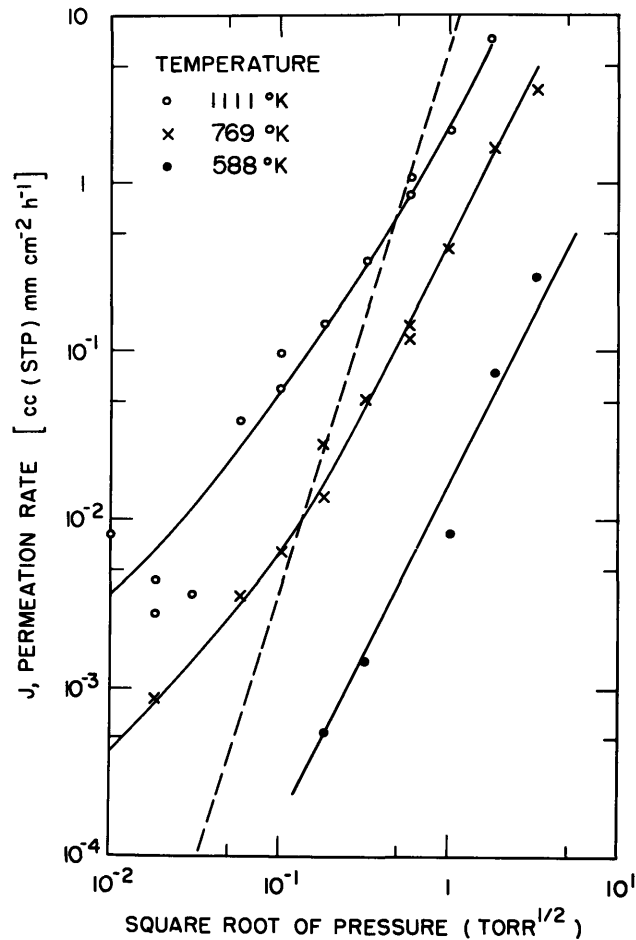


Fig. II-3. Pressure dependence of the rate of permeation of hydrogen through niobium. The dashed line corresponds to an ablayer hydrogen concentration of 0.1 at. %.

of hydrogen is controlled by some mechanism other than the simple diffusion of hydrogen through the bulk of the membrane. There are two possibilities. First, according to existing solubility data<sup>1, 10</sup> the H-Nb system does not behave as an ideal dilute solution over the entire pressure and temperature range of this investigation. Because of this, we should not expect the permeation rate to vary in the manner predicted by the common permeation equation (Eq. 2) for those combinations of pressures and temperatures that resulted in a nondilute solution. In Fig. II-3 the dashed line corresponds to the loci of points representing an H to Nb atomic ratio of  $1 \times 10^{-3}$  (0.1 at. %). Since niobium is an exothermic absorber of hydrogen, the solubility of H in Nb decreases with increasing temperature. Consequently, for pressures and temperatures where an ideal dilute solution exists, namely  $x < 1 \times 10^{-3}$ , the dependence of  $J$  on  $p_1$  as predicted by Eq. 2 approaches the limit  $J/p^{1/2} = \text{constant}$ . This illustrates the inherent error in blindly using the  $p^{1/2}$  rule in extrapolating data to low pressures. For example, if the data of

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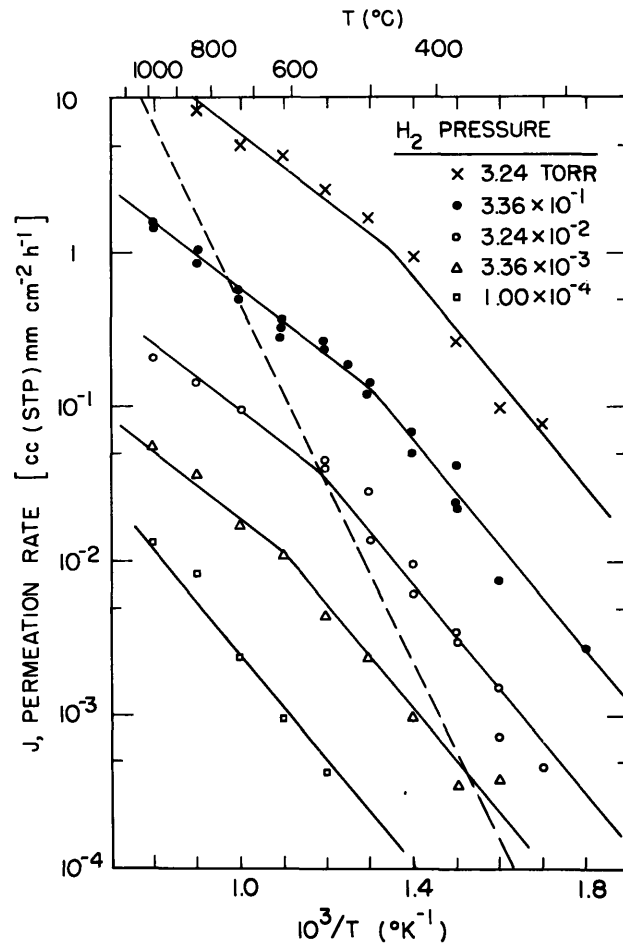


Fig. II-4. Temperature dependence of the rate of permeation of hydrogen through niobium. The dashed line corresponds to an ablayer hydrogen concentration of 0.1 at. %.

Rudd et al.<sup>9</sup> for  $T = 1250^\circ\text{K}$  and  $p_1 = 760$  Torr are extrapolated to  $p = 1.0 \times 10^{-3}$  Torr using the  $p^{1/2}$  rule, the resulting estimate is greater by approximately a factor of seven than our corresponding measurement. Since the dashed line in Fig. II-4, which again corresponds to the loci of points representing a hydrogen concentration of 0.1 at. %, does not coincide closely with the knee in the plot of  $\log_{10} J$  vs  $1/T$ , we must conclude that this anomaly does not appear to be simply the result of deviations from ideal dilute solution behavior.

The second possibility is that surface impurities may have reduced the permeation rate as a result of surface processes such as adsorption, penetration, and desorption. This conclusion is based on: (i) Bradley and Stickney's determination<sup>6</sup> by Auger electron spectroscopy that carbon and sulfur impurities were present on the low-pressure surface of their Nb membrane. (ii) Several reports<sup>10, 12, 13</sup> showed that the rate of absorption or desorption of hydrogen by niobium depends strongly upon the surface

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preparation process and on the history of the sample. For example, Oakwood and Daniels<sup>12</sup> found that the rate of absorption increased as much as an order of magnitude when the surface was abraded rather than chemically etched. On this basis, it is very probable that our results were influenced by surface impurities. Because of the lack of more reliable data in the pressure and temperature ranges where an ideal dilute solution of H in Nb exists, especially for clean surfaces with driving pressures less than  $5 \times 10^{-4}$  Torr, we cannot completely rationalize our data on the basis of an analysis similar to that presented in this report.

### 3. Conclusion

The results of our present experiment appear to indicate that the permeation of hydrogen through niobium is strongly affected by surface impurities, deviations from ideal dilute solutions, and possibly by some other mechanism still to be determined. We base this conclusion on the fact that in general  $J$  was not proportional to the square root of the driving pressure and that  $\log J$  did not vary linearly with inverse temperature. Furthermore, our analytical results, together with our experimental results, demonstrate that great care must be taken in extrapolating existing experimental data to the low pressures that are associated with some applications, since surface processes should greatly influence the permeation rate.

We are planning to perform additional experiments employing deuterium and a niobium membrane with a "clean" downstream surface in order to answer some of the questions posed by our present data.

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