THE PERMEATION OF HYDROGEN
THROUGH HASTELLOY B

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ABSTRACT

The flux of hydrogen gas through Hastelloy B, hot forged to 20% reduction, was determined as a function of membrane thickness, pressure differential, and temperature. The experimental data were fitted to the following equation:

$$J = \frac{16.79 P^{1/2}}{X} \exp\left(\frac{-8470}{T}\right)$$

where

J = flux (cc at STP/(cm²-hr)

P = pressure (atmospheres)

X = membrane thickness (mm)

T = temperature (°K)

I. INTRODUCTION

The process of permeation of a solid by a gas is composed of a series of individual processes. The gas must first be adsorbed on the surface of the metal, and this may or may not involve a dissociation. In the case of the permeation of metals by hydrogen, the mechanism is generally dissociation on the surface and solution as atoms. Following this, the molecules, or atoms, diffuse through the solid with their rate of transport being characterized by the familiar Fick's Laws. The final step is escape from the downstream side of the solid, possibly followed by recombination of the diffusing species.

Because of the relatively complex nature of the numerous factors in the permeation process, one does not often completely investigate the mechanism of the individual steps and characterize them in terms of measurable quantities. The conventional approach; which is used here, is to measure the total flux of gas, at steady state conditions, through a membrane. The flux, under stated conditions, is frequently called the permeability. Permeability is not really a fundamental quantity, but is, nonetheless, a very useful engineering property of the system.

The dependence of the flux (or permeability) on membrane thickness, pressure differential across the membrane, and temperature are empirically determined for the range of these properties of interest. These dependencies are expressed in an empirical equation, which then is useful for calculating fluxes at intermediate conditions.

II. APPARATUS AND METHODS

Vacuum cast Hastelloy B ingots were obtained from National Research Corp., Cambridge, Massachusetts. The analysis of the material is given in Table I.

TABLE I
ANALYSIS OF HASTELLOY B STOCK

Element	wt %
Ni	Balance
Mo	28.14
Fe	5.91
Cr	0.94
Mn	0.36
C	0.093
Si	0.005

The photomicrograph in Figure 1 shows the structure of the Hastelloy B diaphragm. As stated, the material had been hot forged to 20% reduction prior to machining, which caused the coarse stringer-like appearance of the second phase. A certain amount of cold-work was present in the material prior to heating, as indicated by the recrystallized grain structure.

5 Sec etch HNO_3 (conc.)

250X

Figure 1. Photomicrograph of Hastelloy B Stock

The ingots had been inspected by X-ray and were found to be free of porosity. The stock was machined to the form of solid cylinders 1.5-in. diam. by 5-in. long. The ends were then bored to leave a diaphragm which is an integral part of the assembly, see Figure 2. The thicknesses and diameters of the diaphragms prepared in this manner are given in Table II. A cap was

Figure 2. Diagram of Permeability Apparatus

TABLE II
DIMENSIONS OF DIFFUSION DIAPHRAGMS

Diaphragm No.	Thickness (in.)	Diameter (in.)
1	0.0950	0.9981
2	0.1307	0.9990

welded to each open end of the diffusion assembly and a stainless steel tube 10-in. long by 3/8-in. OD was welded to each cap. A 1/8-inch thermal well was drilled to a point near the diffusion membrane for a thermocouple. The entire assembly was mounted into a resistance furnace, shown schematically in Figure 2.

Tank hydrogen was fed successively through a catalytic purifier, a three-foot column of calcium hydride, and finally through a twelve-inch titanium hydride getter maintained at 900 to 1000°C. After leaving the titanium hydride getter, the gas entered a palladium coil housed in the upstream side of the diaphragm. The hydrogen so purified diffused through the diaphragm membrane and was pumped from the downstream side by means of a Toepler pump into a calibrated volume. The quantity of gas collected was measured by means of a vernier attached to a mercury manometer. The readings were corrected for any change in temperature of the atmosphere surrounding the calibrated volume. This change in temperature was read to $\pm 0.5^\circ\text{C}$. A dry-ice-acetone cold trap was placed between the pump and the exit tubes of the diaphragms to prevent the migration of mercury vapor.

The heating of the furnaces was regulated by external resistances. The temperature of the furnaces was controlled to $\pm 1^\circ\text{C}$ by means of Wheelco Capiciline temperature controllers.

The hydrogen pressure on the upstream side of the diffusion membrane could be read by use of a Burdon type pressure gauge. The pressure of the hydrogen, after diffusing through the palladium coil and filling the upstream side of the diaphragm assembly, was controlled by permitting it to build up in excess of the desired level, then bleeding off into a long mercury column. By raising or lowering the column, the pressure could be very accurately controlled and the upstream side of the diaphragm assembly could be constantly flushed thus removing any foreign gases which might have accumulated due to reduction, when heat and hydrogen were first applied. Prior to use of hydrogen both upstream and downstream sides of the diaphragm were evacuated. The vacuum on the upstream side was read on the Burdon gauge, on the downstream by a McLeod gauge. The upstream side maintained a vacuum of 30 in. for a period

of 7 days, whereupon hydrogen was introduced and diffusion runs started. A vacuum of 10^{-6} mm of mercury was obtained by the glass vacuum system in the usual manner, by use of mechanical and diffusion pumps combined.

The Hastelloy B diaphragms were heated to a temperature of 800°C and required approximately 48 hours to outgas. After outgassing, a blank run was initiated. The blank run was stopped after 72 hours. No detectable quantity of gas could be read on the recorder at this time. This means that the error in observed specific rate is less than $0.000012 \left[(\text{cc at STP/hr}^{-1}) / (\text{cm}^2 / \text{mm}^{-1}) \right]$. Following this the temperature was lowered to 760°C and runs were made at 1.1, 1.5, and 2.0 atmospheres. The temperature was subsequently adjusted to 700, 640, and finally 820°C .

III. EXPERIMENTAL RESULTS

The complete tabulation of experimental results for the two membranes of Hastelloy B tested are given in the Tables III and IV. The dependence of the permeability on membrane thickness, pressure differential, and temperature are shown below.

A. MEMBRANE THICKNESS

If the permeation process is diffusion limited and not controlled by surface effects, the flux $\left[\text{cc at STP}/(\text{cm}^2\text{-hr}) \right]$ is inversely proportional to membrane thickness X . As a first approximation, the following function at constant pressure-temperature differential is assumed:

$$J = \frac{k}{X} \quad \dots(1)$$

where

J = flux

x = membrane thickness (mm)

and

k = proportionality constant.

This will now be compared with the experimental data.

In Table V, the value of the constant k from Equation 1 is given for different experimental conditions. It may be observed that k is the same for either membrane at the same experimental temperature and pressure, which confirms Equation 1 and indicates the absence of surface controlling factors.

TABLE III

RATE OF HYDROGEN PERMEATION THROUGH HASTELLOY B

(Diaphragm 1: thickness = 0.0950 in. ; diameter = 0.09981 in.)

Temperature (°C)	Pressure (Atm)	Rate (cc at STP/hr)	Flux [cc at STP/(cm ² -hr)]	
			Actual	Calculated
640	1.1	0.385	0.0763	0.0826
		0.382	0.0767	
		0.384	0.0761	
	1.5	0.457	0.0905	0.0964
		0.438	0.0868	
		0.478	0.0947	
	2.0	0.524	0.1038	0.1113
		0.524	0.1038	
		0.549	0.1088	
700	1.1	0.674	0.1335	0.1456
		0.674	0.1335	
		0.673	0.1333	
	1.5	0.803	0.1591	0.1700
		0.802	0.1589	
		0.785	0.1555	
	2.0	0.915	0.1813	0.1963
		0.915	0.1813	
		0.901	0.1785	
760	1.1	1.125	0.2229	0.2404
		1.139	0.2256	
		1.169	0.2316	
	1.5	1.398	0.2769	0.2807
		1.346	0.2666	
		1.376	0.2726	
	2.0	1.549	0.3069	0.3241
		1.554	0.3078	
		1.560	0.3090	
820	1.1	1.772	0.3510	0.3758
		1.751	0.3469	
		1.801	0.3568	
	1.5	2.101	0.4162	0.4387
		2.030	0.4021	
		2.077	0.4115	
		2.081	0.4122	
	2.0	2.375	0.4705	0.5066
		2.383	0.4721	
		2.376	0.4704	

TABLE IV

RATE OF HYDROGEN PERMEATION THROUGH HASTELLOY B

(Diaphragm 2: thickness = 0.1307 in.; diameter = 0.9990 in.)

Temperature (°C)	Pressure (Atm)	Rate (cc at STP/hr)	Flux [cc at STP/cm ² -hr]	
			Actual	Calculated
640	1.1	0.281	0.0556	0.0533
		0.287	0.0568	
		0.285	0.0564	
	1.5	0.343	0.0678	0.0622
		0.381	0.0753	
		0.349	0.0690	
	2.0	0.413	0.0817	0.0718
		0.379	0.0749	
		0.362	0.0716	
700	1.1	0.501	0.0991	0.0940
		0.509	0.1007	
		0.492	0.0973	
	1.5	0.584	0.1155	0.1097
		0.573	0.1133	
		0.577	0.1141	
	2.0	0.657	0.1299	0.1267
		0.667	0.1319	
		0.675	0.1335	
760	1.1	0.845	0.1671	0.1552
		0.845	0.1671	
		0.841	0.1663	
	1.5	0.987	0.1953	0.1813
		1.000	0.1977	
		0.989	0.1956	
	2.0	1.155	0.2284	0.2093
		1.159	0.2292	
		1.142	0.2258	
820	1.1	1.358	0.2739	0.2426
		1.356	0.2681	
		1.351	0.2616	
	1.5	1.540	0.3045	0.2833
		1.532	0.3029	
		1.535	0.3035	
	2.0	1.700	0.3362	0.3270
		1.695	0.3352	
		1.692	0.3346	

TABLE V
THE PROPORTIONALITY CONSTANT BETWEEN FLUX
AND MEMBRANE THICKNESS

T (°C)	P (atm)	k $\frac{\text{cc at STP} - \text{mm}}{\text{cm}^2 - \text{hr}}$	
		Membrane 1	Membrane 2
640	1.1	0.184	0.186
	1.5	0.218	0.222
	2.0	0.255	0.253
700	1.1	0.322	0.329
	1.5	0.381	0.380
	2.0	0.435	0.439
760	1.1	0.547	0.553
	1.5	0.657	0.652
	2.0	0.744	0.758
820	1.1	0.849	0.890
	1.5	0.991	1.009
	2.0	1.137	1.115

B. PRESSURE DIFFERENTIAL

The flux of a diatomic gas through a membrane is generally proportional to the square root of the pressure difference on the membrane. For a diffusion controlled process the flux is proportional to the concentration gradient, which in turn is proportional to the difference in the square roots of the upstream and downstream pressures according to Sievert's Law. The pressure dependence of the flux should, therefore, mathematically take the form of Equation 2 at constant temperature and membrane thickness and with downstream pressure equal to zero.

$$J = k' P^{1/2} \quad \dots (2)$$

where

$$J = \text{flux} \left[\frac{\text{cc at STP}}{\text{cm}^2 - \text{hr}} \right]$$

k' = proportionality constant

P = upstream pressure (atm)

Taking logarithms of both sides gives Equation (3):

$$\log J = \log k' + 1/2 \log P \quad \dots (3)$$

If one were to plot $\log J$ as a function of $\log P$ for a given temperature and membrane thickness and find that the slope was equal to $1/2$, then Equation 2 would be verified. In Figure 3, the data from Membrane 1 are plotted as $\log J$ vs $\log P$. The slopes of the various temperature lines are very nearly $1/2$, verifying Equation 2. A similar result was obtained from Membrane 2.

Figure 3. Log of Flux vs Log of Pressure for Membrane 1 at Four Temperatures

C. TEMPERATURE DEPENDENCE

If the permeation is primarily a diffusion controlled process, as is becoming increasingly evident from the dependence of flux on the reciprocal thickness and the 1/2 power of the upstream pressure, then the temperature dependence should follow the familiar Arrhenius relationship. In other words, the natural logarithm of the flux should be proportional to the reciprocal absolute temperature at constant membrane thickness and pressure differential.

$$J = k'' e^{-\frac{A}{T}} \quad \dots (4)$$

or

$$\ln J = \ln k'' - \frac{A}{T} \quad \dots (5)$$

where

$$J = \text{flux} \frac{\text{cc at STP}}{\text{cm}^2/\text{hr}}$$

k'' , A = proportionality constants

T = temperature ($^{\circ}\text{K}$)

If the plot of $\ln J$ vs $1/T$ does yield a straight line, Equation 5 is confirmed. This function is plotted in Figure 4 for three different pressure differentials on Membrane 1. The lines are indeed straight.

Figure 4. $\ln J$ vs Reciprocal Temperature for Membrane I at Three Pressures

D. SUMMARY OF RESULTS

In the preceding paragraphs it has been shown that:

$$J = f(X^{-1}, P^{1/2}, e^{-A/T}) \quad \dots (6)$$

or

$$J = \frac{B}{X} P^{1/2} e^{-A/T} \quad \dots (7)$$

The complete set of experimental data were fitted to an equation of this form using a machine program based on a least squares fit, and the constants A and B were evaluated. The final equation which best represents the data is:

$$J = \frac{16.79 P^{1/2}}{X} \exp\left[\frac{-8470}{T}\right]$$

The fit of the data to this equation is illustrated by Tables III and IV, where the calculated fluxes are compared to measured fluxes. It should be noted that the calculated values are slightly high for the thinner diaphragm and slightly low for the thicker diaphragm. It would require measurements with a greater number of membranes to fully confirm the effect of membrane thickness on flux.