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PERMEATION OF HYDROGEN THROUGH
METALS

AEC Research and Development Report

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PERMEATION OF HYDROGEN THROUGH
METALS

By
R. W. WEBB

ATOMICS INTERNATIONAL
A DIVISION OF NORTH AMERICAN AVIATION, INC.

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ABSTRACT

The permeability of hydrogen through those metals being considered for use in SNAP reactor systems must be known in order to predict hydrogen mobility and migration in the NaK primary coolant system of the reactors. Of particular concern is the amount of hydrogen which will migrate into the mercury boiler loop.

Data were gathered from the literature on the flux of hydrogen gas permeating various metals, and experiments were made with a hydrogen-sensitive mass spectrometer to collect additional data. The high-pressure data were fitted to the equation

$$\phi = \frac{CP^{1/2}}{x} \exp\left(-\frac{Q}{RT}\right) ,$$

which relates the flux to the hydrogen pressure, the metal thickness, and the activation energy for diffusion. Data on the low-pressure hydrogen permeation of Hastelloy N were not sufficient to justify a curve fitting. However, it was evident that Sievert's law ($\phi = KP^{1/2}$) does not hold below about 10 mm Hg, but that the permeation equation takes the form of:

$$\phi = \frac{CP}{x} \exp\left(-\frac{Q}{RT}\right) .$$

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I. INTRODUCTION

The SNAP reactor systems use a hydrogen-moderated, Zr - 10 U alloy as the fuel material, operating between 1050 and 1550°F. Hydrogen retention in the fuel presents a formidable problem, especially at elevated temperatures, since all known materials are permeable to hydrogen to some extent. Excessive loss of hydrogen from the core would result in a serious reduction in reactor control and lifetime capabilities. Effective hydrogen barrier materials have been developed which will reduce hydrogen loss from the reactor to an acceptable level; however, small amounts of hydrogen will permeate the fuel element cladding and will subsequently enter the liquid metal (NaK) coolant channels. Hydrogen transport from the NaK to the mercury loop of the SNAP 8 and other Mercury Rankine Conversion Systems, by permeation through the mercury-NaK heat exchanger, may result in degradation of system performance. Therefore, knowledge of hydrogen permeation kinetics through metallic piping is invaluable in helping to predict overall system performance. A guide to predict general hydrogen distribution in the overall SNAP system is obtained by determining hydrogen loss rates to space, and hydrogen concentrations in the NaK and in the mercury.

Existing data on the rates of hydrogen permeation through structural materials were reviewed and some obvious gaps were filled by experimental studies at Atomics International. As shown in Figure 1, pure metals show a wide range of permeability to hydrogen. Niobium and palladium are extremely permeable, whereas molybdenum and tungsten offer substantial resistance to hydrogen flow. Iron and nickel possess intermediate permeation rates and most of their alloys fall within an extremely narrow permeation range which, as a first approximation, is a weighted average of the permeation of the individual components.

Most metals offer no great potential as hydrogen barriers, but the proper choice of material could solve some problems by offering a partial resistance to hydrogen flow or by acting as a "hydrogen window" to dissipate hydrogen gas from specific areas within the reactor system. The purpose of this report is to document available information on activation energies for permeation of hydrogen through metals of interest to the SNAP program. A modest experimental program was also undertaken to supplement and verify data for a selected group of alloys.

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Figure 1. Permeation Rate vs Temperature

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II. GENERAL THEORY OF PERMEATION

The permeation of gases through metal is a relatively complex process which, for ease of measurement, is defined as the amount of gas which migrates from the gas phase on one side of a membrane to the gas phase on the other side. This permeability (or flux) is not a fundamental quantity, but is a resultant product of several interrelated processes. Empirically, the dependencies of permeability can be expressed in terms of membrane thickness and pressure differential across the membrane by the familiar Fick's law, and to temperature by the Arrhenius rate theory.

Fick's first law states that the quantity of diffusing substance, ϕ , which passes per unit time through unit area of a plane at right angles to the direction of diffusion, is proportional to the concentration gradient of the diffusing substance. If C denotes concentration and x denotes the direction of diffusion, then

$$\phi = -D \frac{\partial C}{\partial X} \quad \dots (1)$$

where D = coefficient of diffusion (cm^2/sec).

Under equilibrium conditions, the rate at which gas enters the metal on the high pressure side and the rate at which it leaves the low pressure side become equal and, similarly, the concentration of dissolved gas in the metal no longer changes with time. If the concentration gradient, $\partial C/\partial X$, is constant it may be rewritten as $(C_o - C_1)/\Delta X$, where C_1 and C_o are the concentration on each side of the membrane and ΔX represents the membrane thickness. Since both sides of the membrane are in equilibrium with the gas phase surrounding it the concentration is related to the gas pressure. For diatomic gases such as hydrogen, nitrogen, and oxygen this relationship is best expressed by Sievert's law: $C = S \sqrt{P}$, where S is the solubility at unit pressure. This relationship is based on the assumption that the gas is dissolved atomically in the metal and the equilibrium equation is:

The mass law constant is then

$$K = \frac{C_H^2}{P_{H_2}}$$

or

$$C_H = \sqrt{KP_{H_2}} \quad \dots(3)$$

The flux, ϕ , may now be expressed in terms of the pressure:

$$\phi = -DS \frac{\sqrt{P_o} - \sqrt{P_i}}{\Delta X} \quad \dots(4)$$

If P_o is maintained at essentially zero, P_i at 1 atm, and ΔX at 1 mm for a 1 cm^2 cross section, then:

$$\phi = DS \quad , \quad \dots(5)$$

or, under these special conditions, the flux or permeability is proportional to both the diffusivity and the solubility.

For this report, the permeability constant has been denoted as C and is in units of $\text{cc(STP)-mm/hr-cm}^2\text{-atm}^{1/2}$. Also, the flux (ϕ) is the permeability at 1 atm pressure and 1 mm thickness.

When thermal conditions change, the rate theory must be applied. The foundation of present rate theory came from Arrhenius, who found that the specific reaction-rate constant for many processes may be expressed in terms of temperature by the equation:

$$K = A \exp(-Q/RT) \quad , \quad \dots(6)$$

or $\ln K$ is a linear function of $1/T$. Q is the slope of such a plot and is regarded as the energy of activation of the reaction.

One of the most frequently used relations in the consideration of chemical equilibria is K, the thermodynamic equilibrium constant. The general free-energy change, ΔF is related to K at equilibrium by

$$\Delta F = -RT \ln K \quad , \quad \dots(7)$$

also, ΔF , or the Gibbs free energy is defined as:

$$\Delta F = \Delta H - T\Delta S \quad , \quad \dots(8)$$

where:

ΔH = enthalpy (cal/mole)

ΔS = entropy (cal/mole-°K)

T = absolute temperature (°K).

Since permeability can be expressed as an equilibrium constant in terms of pressure, it follows that:

$$\Delta F = -RT \ln P \quad , \quad \dots(9)$$

and further, by combining Equation 9 with Equation 8 we get:

$$-RT \ln P = \Delta H - T\Delta S \quad , \quad \dots(10)$$

where: $\Delta H \equiv Q$ (activation energy for diffusion, cal/mole).

Rearranging Equation 10 gives

$$\ln P = -\frac{Q}{RT} + \frac{\Delta S}{R} \quad . \quad \dots(11)$$

An Arrhenius plot of $\ln P$ vs $1/T$ then results in a straight line of slope (Q) and an intercept at $1/T = 0$ of $\Delta S/R$.

To obtain a better fundamental understanding of the complex permeation process, the individual processes will be discussed and examples given where each process can be the rate-limiting or rate-controlling step in the overall

permeation process. For this discussion, the rate-controlling step is defined as the slowest step in the permeation process under equilibrium conditions.

The individual steps in the permeation process act at the entrance surface, in the bulk of the metal, and at the exit surface. The steps include the following:

- 1) Entrance surface adsorption, dissociation, and solution
- 2) Bulk diffusion
- 3) Exit surface desorption and recombination.

A. ENTRANCE SURFACE

Where the entrance surface gas pressure is very low, or where the temperature of the entrance surface is below the temperature at which the gas will dissociate,⁽¹⁾ the first step in the permeation of gases through metals can be considered the rate-controlling step. The permeation of diatomic gases through metals (at moderate pressures) depends on the gas solubility, which varies as the square root of pressure (Sievert's law). If the pressure is reduced to such a point that the active surface is no longer completely covered by the gas, the pressure dependence tends to become linear with a theoretical fit to the Langmuir chemisorption formula:

$$\theta = \frac{bp}{1 + bp} \quad , \quad \dots(12)$$

where

θ = fraction of surface covered

p = gas pressure

b = constant.

Most metals do not pass appreciable quantities of gas if exposed to molecular hydrogen below about 200°C. If, however, atomic hydrogen is supplied to the metal surface by reaction with an acid, by electrolysis, or by ionization, rapid permeation occurs even at room temperature.⁽¹⁾ Hydrogen atoms can easily dissolve in metal, diffuse, and readily leave the exit surface to recombine as molecules. Dissociation of molecules into atoms on the entrance surface is, for this low-temperature example, the process which determines the permeation velocity of molecular hydrogen.

The solubility of gas in the metal at, or near, the entrance surface is also an important consideration in determining the rate at which the permeation process will occur. This is substantiated⁽²⁾ by the fact that there is no known case of a gas diffusing through a metal in which it is not soluble. Baukloh and Kayser⁽⁸⁾ report that nickel is impervious to helium, neon, argon, and krypton. Ryder⁽⁹⁾ found no permeation of iron by argon.

B. DIFFUSION

Diffusion of gases through metals occurs by a motion of their atoms (or ions) along interstitial sites in the metal. Interstitial diffusion is not affected by grain boundaries, as verified by C. A. Edwards,⁽³⁾ who found no difference between the rate of hydrogen diffusion through single crystal and polycrystalline iron.

The temperature dependence on diffusion is brought about by vibrational excitation of the atoms which expands the lattice and allows gas atoms to "jump" from one interstitial site to another. Only those atoms which possess a very large energy with respect to the average energy of the atoms can make this jump, since repulsive forces must be overcome to force the foreign atom through the energy barrier which binds the metal together. This can be deduced from Figure 1, where the permeation constant decreases as the melting point of the metal increases. For example, tungsten (m.p. 3653°K) is less permeable than molybdenum (m.p. 2873°K).

For metals,⁽¹⁰⁻¹²⁾ the permeation rate of gases has been found to be inversely proportional to the metal thickness, which implies that diffusion through the crystal lattice is the rate-controlling process. Additional evidence that diffusion can be a rate-controlling step was obtained from measurements of the hydrogen permeability of complex membranes Cu-Pd-Cu and Pd-Cu-Pd.⁽¹⁹⁾ At 400°C, the permeability of palladium for hydrogen is about 10^5 times greater than that of copper. If the total thickness of the copper in both complex membranes is constant, the same permeation rates would be expected for both if diffusion is the rate-controlling step, rather than a process on one of the boundaries between gas and metal. If adsorption were limiting, very divergent permeabilities must be observed. Indeed, the permeabilities were found to be the same.

C. EXIT SURFACE

An example of a case in which the reaction at the exit surface determines the permeability is the passage of hydrogen through palladium.⁽¹⁾ Palladium in contact with molecular hydrogen can take appreciable quantities of this gas at room temperature. The velocity of diffusion in palladium is quite high, but the hydrogen is unable to leave the metal if below 100°C. Therefore, a much large activation energy is required at the exit surface than is required for either adsorption or diffusion. This high activation energy is apparently required for the recombination of the adsorbed atoms on the surface. At room temperature, palladium can lose hydrogen if it is placed in an oxygen atmosphere. Apparently this is brought about by a reaction of the oxygen with the hydrogen atoms on the surface.

III. EXPERIMENTAL PROCEDURE

A. APPARATUS AND PROCEDURES USED BY OTHER INVESTIGATORS

In general, either flat disc or cylindrical tube specimens⁽¹³⁾ are used to investigate hydrogen permeability of metals. Gas flow rates are observed by allowing the permeating gas to collect in a calibrated volume over a definite time period. A mercury column, or a multirange McLeod gauge, is commonly used to measure the gas pressure on the downstream side of the membrane, which permits calculations of gas volume flow per unit time.

Due to the complex nature and numerous variables in the permeation process, only the total flow of gas through the membrane is measured. The dependence of permeability on temperature, pressure, and membrane thickness is expressed empirically, so that a knowledge of these parameters is all that is required for calculating the quantities of hydrogen which will permeate various metals under most conditions.

The permeability equation normally used to evaluate the quantity of gas permeating a metal barrier is of the form:

$$F = \frac{CA}{x} \left(P_1^{1/2} - P_2^{1/2} \right) \exp \left(- \frac{Q}{RT} \right) t \quad , \quad \dots (13)$$

where:

F = the quantity of gas permeating (cc at STP)

C = permeation constant of gas-metal system [cc(STP)-mm/hr/cm²-atm^{1/2}]

A = area of metal barrier (cm²)

P₁ = upstream H₂ pressure (atm)

P₂ = downstream H₂ pressure (atm)

Q = activation energy of diffusion (cal/mole)

x = thickness of metal barrier (mm)

R = gas constant (cal/mole-°K)

T = absolute temperature (°K)

t = time (hr)

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Figure 2. Permeation Apparatus

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Figure 3. Typical Permeation Membranes

B. APPARATUS AND PROCEDURES USED IN THIS INVESTIGATION

1. Membrane and Furnace System

In this investigation, cylindrical membranes were used exclusively for the following reasons:

- 1) There are generally no welds or seals in the hot zone that may develop leaks.
- 2) There is no adjoining material which could add to or change the overall flow through the membrane, thereby clouding the results.
- 3) A much larger permeating area can be used, which tends to minimize inherent errors due to low flow rates, surface films, and impurities. It is easy to compensate for errors due to thermal gradients along the membrane, as will be shown in a later section.

The apparatus used for this study is shown schematically in Figure 2. The test membrane was a thin-walled tube of the material to be tested. Either metal or glass closures were used as an integral part of the membrane; depending on the availability of bar stock, the machineability, and the weldability of the particular metal being investigated. If metal end caps were used, a weld would be included in the hot zone in order to obtain a longer isothermal test section (Figure 3). If, however, as was the case for tungsten, end caps were not practicable, a glass-to-metal seal technique was employed (Figure 3). The glass-to-metal seal was made by bonding a relatively soft uranium glass to both ends of the tungsten tube. One end was sealed by closing the glass, and the other end was attached to a Kovar seal and subsequently welded to a Type 304 stainless steel hydrogen inlet tube. Since dissimilar materials were involved, both ends of the tungsten tubing were maintained at a temperature sufficiently low so as not to interfere with permeation results. The main drawback with this arrangement was that a relatively large percentage of both ends of the sample were maintained in a nonisothermal condition. Methods for correction of this condition will be discussed later.

Membranes used in this study were generally about 5/8 in. in diameter by 12 to 20 in. long. All membranes had a 3/16-in. -diameter hydrogen inlet tube welded to one end, which further aggravated the temperature-gradient problem

since the hydrogen inlet tube had to be maintained at less than 700°F to prevent excessive hydrogen loss through the inlet tube walls.

The membrane assembly was enclosed in a quartz vacuum system (Figure 2) surrounded by a resistance-wound tube furnace equipped with temperature-profile-measuring thermocouples. Hydrogen was admitted to the inside of the test membrane and that which permeated the metal was continuously monitored by a hydrogen-sensitive mass spectrometer.

2. Mass Spectrometer

A Consolidated Electrodynamic Corporation Model 24-210B helium-hydrogen leak detector was used in these studies (Figure 4). This instrument is capable of sensing hydrogen flows as low as 5×10^{-5} atm-cc/hr-div. Hydrogen molecules, entering the leak detector vacuum system, flow into the analyzer section where they are bombarded with electrons emitted from an incandescent tungsten filament. The resulting charged particles are then accelerated into a magnetic field, where they are separated into groups according to their atomic mass.

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Figure 4. Mass Spectrometer System

Measurement of the relative intensities of the groups is accomplished by collecting a group of interest (H_2 , in this case) and amplifying the signal in a dc-amplifier system. The amplified signal can then be continuously monitored on an output meter and/or strip chart recorder.

This type of instrument is heavily dependent on an outside calibration system, since the leak detector is a comparator, and not a direct measurement device. The calibration system employed three hydrogen-filled glass leaks, previously standardized by a multirange McLeod gauge. Each day, the hydrogen flows from these three standard leaks were individually monitored on the mass spectrometer until steady-state flow rates were observed. A plot of standard-leak flow rate vs spectrometer meter output resulted in a calibration curve which was used to compute comparative flow rates through membranes from the meter output.

Using this procedure, the mass spectrometer has been used successfully as an analytical instrument to measure flow of hydrogen by the comparative method. The accuracy of data taken by this method is $\pm 5\%$.

3. Temperature Compensation Techniques

For this study, the downstream pressure (P_2 , Equation 1) was maintained at a vacuum of 10^{-3} torr or better, so that, for all practical purposes, $P_2 = 0$. The permeation equation (Equation 1) may then be rewritten and rearranged to the form:

$$\phi = \frac{CP_1^{1/2}}{x} \exp\left(-\frac{Q}{RT}\right) \quad , \quad \dots (14)$$

where:

$$\phi = \text{flux [cc(STP)/hr-cm}^2\text{]} \quad ,$$

or

$$\phi = \frac{CP_1^{1/2}}{x} \exp\left(-\frac{Q}{RT}\right) \quad , \quad \dots (15)$$

where

P = hydrogen pressure differential (atm).

Examination of Equation 15 shows that, for any particular test, C , x , Q , and R are constants, and the measured flow is dependent on only two parameters:

temperature and pressure. If the pressure is maintained constant, the flow becomes simply a function of the absolute temperature, and if one assumes isothermal conditions, a plot of the logarithm of the flux as a function of the reciprocal absolute temperature yields a linear relationship of slope Q . Although Equation 15 is set up for the isothermal case, an acceptable approximation under nonisothermal conditions can be obtained by graphically integrating any test area in a nonisothermal region and assigning a weighting factor for flow in that temperature zone.

Recently, a more sophisticated and reliable method has been developed for analyzing permeation data, using a digital computer. The program written for this study uses the following logic to compute values for the activation energy of diffusion, (Q) (slope of $\ln \phi$ vs $1/T$ plot):

1) Let $\phi_1 = H_2$ flux at T_1

$\phi_2 = H_2$ flux at T_2

2) Let $T_1 = f_1(x)$ = temperature gradient along membrane at higher test temperature

$T_2 = f_2(x)$ = temperature gradient along membrane at lower test temperature.

Figure 5 shows a typical temperature gradient used in this study.

3) Using Equation 15, we divide ϕ_1 by ϕ_2 to obtain

$$\frac{\phi_1}{\phi_2} = \frac{\frac{CP^{1/2}}{x} \exp(-Q/RT_1)}{\frac{CP^{1/2}}{x} \exp(-Q/RT_2)}, \quad \dots (16)$$

which reduces to

$$\frac{\phi_1}{\phi_2} = \frac{\exp(-Q/RT_1)}{\exp(-Q/RT_2)} \text{ or } \frac{\phi_1}{\phi_2} - \frac{\exp(-Q/RT_1)}{\exp(-Q/RT_2)} = 0 \quad \dots (17)$$

The temperature gradients, $f_1(x)$ and $f_2(x)$, are then linearly integrated on the computer, and values for Q are automatically substituted into the temperature-compensated equation until the equation is satisfied. This method has proven very satisfactory in the interpretation of hydrogen permeation data through metal membranes.

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Figure 5. Typical Temperature Profile

TABLE 1
ACTIVATION ENERGIES FOR DIFFUSION AND
PERMEATION CONSTANTS

$$\left[\phi = \frac{CP^{1/2}}{x} \exp\left(-\frac{Q}{RT}\right) \right]$$

Metal	Reference	Q (cal/mole)	C
			$\left[\frac{\text{cc(STP)-mm}}{\text{hr-cm}^2\text{-atm}^{1/2}} \right]$
Hastelloy N	AI*	13,800	190
Hastelloy B	16	16,675	1,810
Nickel	1, 2, 15, 17	13,400	1,000
Iron	1, 2, 17	9,100	144
Type 304 SS	AI,* 17	16,100	850
Type 316 SS	13, 15	16,075	1,526
Type 321 SS	13, 15	16,075	1,526
Type 430 SS	15	11,200	360
PH15-7Mo SS	AI*	20,000	7,800
Haynes 25	AI,* 17	15,100	327
Molybdenum	2, 15, 17	20,100	950
Tungsten	AI,* 17	29,340	1,840
Niobium	17, 18	3,430	1,040
Platinum	1, 2	18,600	1,840
Palladium	1	4,500	6,100

*This Work

IV. EXPERIMENTAL RESULTS

A. HIGH PRESSURE

In this study, no attempt was made to verify the results of other investigators as related to the pressure dependence or membrane thickness dependence of hydrogen permeation. It suffices to say, that for all materials tested, pressure dependency followed Sievert's law:

$$\phi = KP^{1/2}, \quad \dots (18)$$

where:

$$\phi = \text{flux [cc(STP)/hr-cm}^2\text{]}$$

K = proportionality constant

P = upstream H₂ pressure (atm).

Also, for most reported results the permeation process has not shown a dependence on surface effects, which indicates the process is diffusion controlled, whereby the flux is inversely proportional to membrane thickness.

Table 1 is a summary of pertinent data on metals of interest to the SNAP project. Listed are the activation energy for diffusion (Q) and the permeation constant (C), which are the only quantities necessary for calculating permeation rates under most normal conditions. The function of the permeation constant (C) is to locate or control the ordinate of a $\ln \phi$ vs $1/T$ plot.

The experimental data are summarized in Figure 1, which shows a plot of flux [cc(STP)/hr-cm²] of hydrogen through various metals as a function of reciprocal temperature. All the data shown are for 1.0 atm hydrogen pressure differential and 1.0 mm membrane thickness. Note that values for ϕ , under these conditions, are exactly the same as the values for C, expressed in [cc(STP)-mm/hr-cm²-atm^{1/2}]. Therefore, both sets of units are plotted in Figure 1.

B. LOW-PRESSURE PERMEATION

Since hydrogen partial pressures in the SNAP primary NaK coolant system are predicted to be extremely low (10⁻³ to 10⁻⁵ atm), an investigation of hydrogen permeation under these conditions was warranted. It has been reported⁽⁵⁻⁷⁾

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Figure 6. Hydrogen Permeation vs Square Root of Pressure at 1200°F (0.010 in. Hastelloy N, direct measurement)

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Figure 7. Hydrogen Permeation vs Square Root of Pressure at 1400°F and 1500°F (0.010 in. Hastelloy N, decay method)

Figure 8. Hydrogen Permeation vs Time at 1400°F (0.010 in. Hastelloy N, $P_0 = 0.125$ atm)

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that, at low gas pressures, the hydrogen permeation rates through metals deviate from Sievert's law ($\phi = KP^{1/2}$). It is postulated that at low pressures the permeation rate is controlled by the metal-surface activity (adsorption) rather than by diffusion mechanisms, and the rate assumes a nearly linear relationship with pressure ($\phi = KP$).

An experiment (Phase I) was conducted on 0.010-in. Hastelloy N to attempt to verify previously reported low-pressure data. Initial studies were conducted by obtaining steady-state hydrogen flow rate as a function of pressure, which was measured by means of a 0 to 15 psi transducer. Results of this run (1200°F) are shown in Figure 6, but it was felt that pressure measurements at the low end of the range were not precise enough. Therefore, a completely different type of permeation test was conducted.

The second approach to the low pressure study was conducted by filling a known volume with an accurately measured volume of hydrogen gas at 0.1 to 1.0 atm pressure. The hydrogen supply to the test specimen (part of the known volume) was then isolated and the permeation rate was monitored, as a function of time, as the pressure inside the membrane decayed. By knowing the starting pressure (P_o), the volume, and the temperature, calculations of pressure at any time could be performed by integrating the hydrogen flow according to the equation:

$$P = P_o - \frac{Kf(t)dt}{V/T} , \quad \dots (19)$$

where

K = proportionality constant

P = pressure at time t (atm)

P_o = starting pressure (atm)

$f(t)$ = hydrogen flow rate (cc/hr)

V = volume of chamber (cc)

T = absolute temperature (°K).

Thus, a plot of hydrogen flux vs pressure could easily be constructed, with values of pressure well below those that were obtainable by the direct measurement technique. Figure 7 shows the results of two runs made, at 1400 and 1500°F,

on similar 0.010-in. Hastelloy N membranes. From Figures 6 and 7, it is obvious that, at low pressures (10 mm Hg), the hydrogen flow rate through Hastelloy N does deviate from the normal square root of pressure relationship. Figure 8 shows a typical plot of hydrogen flow vs time obtained in this experiment.

C. RELATION BETWEEN PERMEATION AND ABSOLUTE MELTING TEMPERATURE

It is interesting to note (from the data displayed in Figure 1) that, for the pure metals which do not form hydrides, the hydrogen permeation rate decreases as a function of the absolute melting temperature. Considerable attention has been given in the literature to the relationship of self-diffusion to melting point.⁽²⁾ Garner⁽¹⁴⁾ stated that lattice mobility relations are governed by, or tend to become operative at, temperatures which represent fairly constant fractions of the absolute melting point of the solid. Such characteristic or "homologous" temperatures are only a general guide to solid state diffusion; but, as such, they are useful. Since the diffusion of hydrogen through metal is by the same general process as solid state diffusion (the movement of atoms from one interstitial site to another), it is proposed that these characteristic temperatures can also be used as a guide for predicting hydrogen diffusion through metals.

Table 2 shows values for such a comparison, computed at one-third the absolute melting temperatures of four different metals. This particular ratio was chosen because it corresponds to the temperature range of the experimental data plotted in Figure 1. It is also a distinct possibility (as deduced from these data) that the activation energy for the diffusion of hydrogen through a nonhydride forming metal is a constant, with respect to the absolute melting temperature.

TABLE 2
RELATIONSHIP OF FLUX AND ACTIVATION
ENERGY TO ABSOLUTE MELTING
TEMPERATURE

Metal	Melting Point (T _m) (°K)	(Q/T _m)*	H ₂ Flux $\left(\frac{\phi/T_m}{3}\right)$
Nickel	1726	7.6	1.1 x 10 ⁻²
Iron	1810	6.0	2.1 x 10 ⁻²
Molybdenum	2873	7.3	1.7 x 10 ⁻²
Tungsten	3653	8.0	1.0 x 10 ⁻²

*Q = activation energy, cal/mole

V. SUMMARY AND CONCLUSIONS

The comparative permeability properties of the materials encompassed in this investigation are summarized, as a function of test temperature or pressure, in Figures 1, 6, and 7. In the low-pressure study, no attempt was made to isolate the influence of surface films on the permeation behavior.

As indicated in Figure 1, pure metals offer a wide range of permeabilities to hydrogen, probably due to the relationship between lattice mobility and the melting temperature of the metal. Some metals, with extremely high permeation velocities at high temperatures, are classed as hydride-formers. One such metal, niobium, exhibits a very pronounced change in activation energy for diffusion at about 900°F. Above this temperature, the niobium acts as a hydrogen "window"; but, below 900°F, niobium begins to hydride, thus causing the observed permeation rate to decrease rapidly.

Iron and nickel-base alloys, for most practical purposes, possess approximately equivalent permeation characteristics, which appear to be independent of composition. A further analysis shows that the permeation rate of an alloy is approximately a weighted average of the permeation rates of the component metals.

It has also been shown that from a plot of $\ln P$ vs $1/T$, the slope is the activation energy for diffusion, and the slope-intercept at $1/T = 0$ is related to the entropy of the diffusion process.

Further, it was concluded that the activation energy for diffusion and the overall permeation velocity of hydrogen through metals represent a fairly constant value when related to a constant fraction of the absolute melting temperature of the metal.

REFERENCES

1. J. D. Fast, "Experiments on the Permeation of Gases Through Metal Walls," Phillips Technical Review, 7 (March 1942) p 74
2. S. Dushman, Scientific Foundations of Vacuum Technique, (John Wiley & Sons, Inc., New York, 1949) p 607
3. C. A. Edwards, Trans A. I. M. E., 117 (1935) p 13
4. F. J. Norton, "Permeation of Gases Through Solids," J. Appl. Phys., 28 (1)(1957) p 34-39
5. D. Randall and O. N. Salmon, "The Permeability of 347 SS to H₂ and Tritium," KAPL 904
6. C. J. Smithells and C. E. Ramsley, Proc. Roy. Soc. London, A, 150 (1935) p 172; 152 (1936) p 706
7. E. O. Brarton and G. F. Clark, Proc. Roy. Soc. London, A, 153 (1935-1936) p 504
8. W. Baukloh and H. Kayser, Z. Metallik., 26 (1934) p 156
9. H. M. Ryder, Elect. F., 17 (1920) p 161
10. V. Lombard, C. Rend., 177 (1923) p 116
11. G. Lewkonja and W. Baukloh, Z. Metallik., 25 (1933) p 309
12. F. M. Johnson and P. Larose, J. Am. Chem. Soc., 46 (1924) p 1377
13. D. W. Rudd and J. B. Vetrano, "Permeability of Metals and Enameled Metals to Hydrogen," NAA-SR-6109 (October 30, 1961)
14. Garner, Chemistry of the Solid State (Butterworth Scientific Publication, 1955) p 307
15. P. S. Flint, "The Diffusion of Hydrogen Through Materials of Construction," KAPL-659 (December 14, 1951)
16. D. W. Rudd, D. W. Vose, and J. B. Vetrano, "The Permeation of Hydrogen Through Hastelloy B," NAA-SR-4898 Rev. (February 1, 1961)
17. E. A. Steigerwald, "The Fermeation of Hydrogen Through Constructional Materials," TRW-ER-4776 (November 30, 1961)

REFERENCES

18. E. A. Steigerwald, "The Permeation of Hydrogen Through Materials for the Sunflower System," TRW-ER-5623 (November 15, 1963)
19. H. W. Melville and E. K. Rideal, Proc. Roy. Soc. A, 153 (1935) p 89
20. L. S. Darken and R. W. Gurry, Physical Chemistry of Metals (McGraw-Hill Book Co., Inc., New York, 1953) p 438