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Phillip J. Smith
Glenn Research Center, Cleveland, Ohio

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National Aeronautics and
Space Administration

Glenn Research Center
Cleveland, Ohio 44135

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Phillip J. Smith
National Aeronautics and Space Administration
Glenn Research Center
Cleveland, Ohio 44135

Summary

Mass transfer of a gas through a selective, solid membrane is an effective method for separation of desired species. This selective permeability is evident in the flow of hydrogen and the isotope deuterium through palladium-silver metal alloy media. In this study, based upon Sieverts's law and the Arrhenius diffusion equation, an empirical correlation was developed to determine the steady-state permeation rate R , dependence on media temperature T , gas supply pressure p_S , and gas backpressure p_B on the lower pressure side. Because of an extensive range of experimental conditions and complete reporting of raw data, the research by Ackerman and Koskinas was used as a source for data allowing empirical equation fitting. Unfortunately, those authors reported best-fit equations that poorly represented their own results. To improve the modeling of the original data and demonstrate the quality of the measurements, the current study develops improved hydrogen and deuterium permeation rate equations:

$$P = 4.22 \times 10^{-6} A [\exp(-704/T)] (\sqrt{p_S} - \sqrt{p_B}) / t \text{ for hydrogen}$$

$$P = 2.12 \times 10^{-6} A [\exp(-468/T)] (\sqrt{p_S} - \sqrt{p_B}) / t \text{ for deuterium}$$

for values of cross-sectional area A (cm²), medium thickness t (cm), pressure p (psia), and temperature T (Kelvin), giving a permeation rate in mole/minute. These equations model permeation rate data more closely than do several other existing literature sources.

Introduction

For hydrogen purification, it is common to investigate palladium as a tool to separate the desired gas from impurities: only hydrogen gas readily passes through bulk palladium metal. Since purification membranes are produced thinly to improve flow rate, palladium is typically alloyed with silver to protect against hydrogen affecting the strength and shape-holding characteristics of the metal (Uemiya et al., 1991). Even though the concentration of silver can approach 60 percent for such a design material, a respectable balance of desirable properties is established to exist for a palladium alloy with 25 percent silver.

There are several existing research articles on this permeation relationship, however, none contain complete tables of all recorded raw data, with the exception of Ackerman and Koskinas (1972). That work appears exceptional in terms of experimental thoroughness, but the reported empirical equation fit does not match well with their own data or that of any other group. No correction of the empirical constants has been published by Ackerman or anyone else. It also remains challenging to obtain a complete derivation of the empirical equation format, which is similar to the one commonly known as the Richardson equation (Richardson, Nicol, and Parnell, 1904).

The purpose of this study is to expressly substantiate the fit equation template, improve the permeation rate model, and compare the results to those previously published. There are four publications that will serve as the primary literature comparisons. These sources are Ackerman and Koskinas (1972), Chabot et al. (1988); Serra et al. (1998); and Yoshida et al. (1981), which will heretofore be referred to as “Ackerman,” “Chabot,” “Serra,” and “Yoshida,” respectively. In these comparison works, each includes a limitation that makes the Ackerman data set emerge as the strongest available for pure hydrogen or deuterium permeation modeling over greater than atmospheric pressure regimes. Yoshida noted that there is a temperature uncertainty of 30 °C in the palladium tube permeation cell, whereas Ackerman claimed a diffusion temperature uncertainty range equal to 20 °C. The hydrogen purification experiments by Chabot and Serra purposely included impurities in the supply stream rather than inputting high-purity gas so the pressure to permeation rate relationship was not direct. Additionally, the maximum supply pressure employed by Yoshida was 290 psi, and Serra limited pressure to 20 psi. Ackerman approached pressure differentials of 1,000 psi.

Symbols used in this report are listed in the appendix.

Theory

With the assumption of steady-state conditions, diffusion flux J is determined from Fick’s first law of diffusion, written as

$$J = -D \frac{dC}{dx} \quad (1)$$

where D is the diffusivity of the gas in the medium, C is the concentration of the gas species, and x is the diffusion length, or position. Rearranging the diffusion equation to

$$J dx = -D dC \quad (2)$$

and assuming linear concentration variation across the diffusion path length allows integration to

$$J(x_B - x_S) = -D(C_B - C_S) \quad (3)$$

where the subscripts S and B refer to the initial position of the diffusion path on the supply pressure side of the medium and the final position on the downstream backpressure side, respectively. This enables evaluation of diffusion flux as

$$J = -D \frac{C_B - C_S}{x_B - x_S} \quad (4)$$

The rate of permeation P is

$$P = JA = -AD \frac{C_B - C_S}{x_B - x_S} \quad (5)$$

where A is the cross-sectional area over which transport is occurring. The diffusion path length is equal to the sample membrane thickness t , such that

$$t = x_B - x_S \quad (6)$$

Concentration of the gas within the metal media results from Sieverts's law, in which

$$C = \sqrt{Kp} \quad (7)$$

where K is the equilibrium constant relevant to the solubility of the gas in the metal and p is the partial pressure of the gas. Substituting Equations (6) and (7) into Equation (5) results in

$$P = JA = -AD \frac{\sqrt{Kp_B} - \sqrt{Kp_S}}{t} = -AD \frac{\sqrt{K} (\sqrt{p_B} - \sqrt{p_S})}{t} \quad (8)$$

In order to account for the activation energy of this equilibrium reaction and quantify the equilibrium constant, it is necessary to derive a relationship for the equilibrium constant from the first law of thermodynamics, which defines the change in internal energy U as follows:

$$dU = \delta Q - \delta W \quad (9)$$

where δQ is the heat supplied to a system and δW is the net quantity of work performed by that system. For an isochoric system in which there is no volume V change, it follows that $dV = 0$ and there is no work performed by the system, so

$$-\delta W = p dV = 0 \quad (10)$$

By the second law of thermodynamics, for a reversible process in a closed system the derivative of entropy dS is equal to

$$dS = \frac{\delta Q}{T} \quad (11)$$

Equation (10) along with a rearranged Equation (11) are substituted for δQ and dW in Equation (9) so that

$$dU = T dS \quad (12)$$

Change in Gibbs free energy G is given by

$$dG = dH - T dS \quad (13)$$

where H is enthalpy, which is further defined as

$$H = U + pV \quad (14)$$

Thus, the derivative of each side of Equation (14) will result in

$$dH = d(U + pV) = dU + d(pV) \quad (15)$$

Via the product rule, it is postulated that

$$d(pV) = p dV + V dp \quad (16)$$

Placement of this result into Equation (15) along with the relation in Equation (12) provides

$$dH = dU - d(TS) = T dS + p dV + V dp \quad (17)$$

Returning to Equation (13), it is possible to simplify this to

$$dG = T dS + p dV + V dp - T dS = V dp \quad (18)$$

with the cancellation of the TdS terms and recalling the isochoric condition.

When assuming applicability of the ideal gas law, volume and pressure are dependent variables related by the equation

$$V = \frac{nRT}{p} \quad (19)$$

where n is the number of moles of gas in the system, which will be constant in steady-state conditions, and R is the ideal gas constant. Replacement of V in Equation (18), and integration from over the interval a to b results in

$$\int_a^b dG = \int_a^b nRT \frac{dp}{p} = nRT \int_a^b \frac{dp}{p} \quad (20a)$$

where a and b are simply two different points within the system.

$$G_b - G_a = nRT \ln(p) \Big|_a^b = nRT [\ln(p_b) - \ln(p_a)] = nRT \ln\left(\frac{p_b}{p_a}\right) \quad (20b)$$

Dividing both sides of the equation by n leads to molar Gibbs free energy G_m from

$$\frac{G_b - G_a}{n} = G_{m,b} - G_{m,a} = RT \ln\left(\frac{p_b}{p_a}\right) \quad (21)$$

By setting p_a equal to the standard-state pressure of 1 bar, by definition $G_{m,a}$ is therefore equal to the standard-state molar Gibbs free energy of formation G^0 . In that form, Equation (21) is generally written as

$$G_m = G^0 + RT \ln\left(\frac{p}{1}\right) = G^0 + RT \ln(p) \quad (22)$$

The change in Gibbs free energy of reaction ΔG is determined by totaling the free energies of reaction products and subtracting the total of free energies for the reactants:

$$\Delta G = \sum G_{m,i, product} - \sum G_{m,i, reactant} \quad (23)$$

which, in the specific case for describing the solubility of one gas species in a metal media, is given by

$$\Delta G = [G_b^0 + RT \ln(p_b)] - [G_a^0 + RT \ln(p_a)] \quad (24)$$

At reaction equilibrium, the change in Gibbs free energy of reaction is equal to 0, and Equation (24) is altered to show

$$G_a^0 - G_b^0 = \Delta G^0 = RT \ln(p_b) - RT \ln(p_a) = RT \ln\left(\frac{p_b}{p_a}\right) \quad (25)$$

Rearranging Equation (25) to solve for pressures gives

$$\frac{p_b}{p_a} = \exp\left(\frac{\Delta G^0}{RT}\right) \quad (26)$$

With an ideal gas, the unitless fugacity coefficient ϕ is equal to 1. By definition, fugacity f must be equal to pressure, as given by

$$f = \phi p = 1p = p \quad (27)$$

Additionally, in gas-phase equilibria, the ratio of reaction product fugacity to reactant fugacity determines the equilibrium constant K , which is

$$K = \frac{f_b}{f_a} = \frac{p_b}{p_a} \quad (28)$$

for a system involving a single gas species passing through a medium with no chemical conversion. Recalling Equation (26), the equilibrium constant is determined to be a function of temperature in the following form:

$$K = \frac{p_b}{p_a} = \exp\left(\frac{\Delta G^0}{RT}\right) \quad (29)$$

In addition to the temperature dependence of the equilibrium constant, diffusivity is also a function of temperature and is typically described by the Arrhenius equation, expressed as

$$D = D_0 \exp\left(\frac{-E_A}{kT}\right) = D_0 \exp\left(\frac{-E_A N_A}{RT}\right) \quad (30)$$

where D_0 is a pre-exponential constant representing the theoretical maximum diffusivity, E_A is the diffusion activation energy, k is the Boltzmann constant, and N_A is the Avogadro constant that is related to the ideal gas law constant through the equation

$$k = \frac{R}{N_A} \quad (31)$$

That relationship enables the substitution enacted in Equation (30). Equations (29) and (30) are substituted into Equation (8) and then simplified to

$$P = AD_0 \exp\left(\frac{-E_A N_A}{RT}\right) \sqrt{\exp\left(\frac{\Delta G^0}{RT}\right)} \frac{\sqrt{P_S} - \sqrt{P_B}}{t} \quad (32a)$$

$$P = AD_0 \exp\left(\frac{\Delta G^0 - 2E_A N_A}{2RT}\right) \frac{\sqrt{P_S} - \sqrt{P_B}}{t} \quad (32b)$$

Data Analysis

It is possible to define a factor β to simplify and replace a grouping of variables in Equation (32b) that includes unknown values, which will be empirically determined. This replacement is

$$\beta = \frac{\Delta G^0 - 2E_A N_A}{2R} \quad (33)$$

so that

$$P = D_0 A \exp\left(\frac{\beta}{T}\right) \frac{\sqrt{P_S} - \sqrt{P_B}}{t} \quad (34)$$

There are two parameters that are constant throughout all Ackerman trials: the effective surface area equal to 208.8 cm² and diffusion path length, or material thickness, equal to 0.012 cm. Initial guesses were provided for the empirical constants in Equation (34) to provide a calculated permeation rate P_{calc} . For each gas species separately, the set of correlation constants for D_0 and β that minimized the residual sum of squares RSS was determined from

$$RSS = \sum_i^N (P_{exp} - P_{calc})^2 \quad (35)$$

where P_{exp} is the experimental permeation rate reported by Ackerman. Empirical constants were developed for the correlations based upon all 63 hydrogen trials and 32 deuterium trials with no exclusions. The constants from the comparison literature sources were converted into the same units as those used by Ackerman.

Results and Discussion

In the case of hydrogen gas, the best-fit values for Equation (34) are shown in Table I (as “Smith”) along with the original Ackerman values and other selected literature constants converted to equivalent units.

The calculated hydrogen permeation rates for each source of fitted constants are compared with the experimental permeation rate in Figure 1. The new constants determined in this report (Smith) result in the smallest discrepancy between experimental and model equation results. The closely linear appearance of the line of parity plot provides visual support for the merit of the Equation (2) correlation with Smith constants. Accuracy for this model is not severely influenced by temperature, so although Ackerman removed certain trials at 300 °C due to some nonlinearity in the results, it is in fact possible to produce an

improved fit equation without any data manipulation. For all temperature and pressure conditions, all other models predict lower permeation rates than were measured. This suggests that equation fits based on experiments at low pressures should not be extrapolated to those at higher pressures. Despite differing experimental set-ups and resultant fit constants, the Chabot and Serra calculated values appear similar. The Yoshida constants result in the worst fit to the data and consistently predict the lowest permeation rates.

TABLE I.—EMPIRICALLY DETERMINED CONSTANTS FOR EQUATION (34) WITH HYDROGEN GAS AND RESIDUAL SUM OF SQUARES RELATIVE TO ACKERMAN EXPERIMENTAL DATASET

Source ¹	Fitted constants		Residual sum of squares, <i>RSS</i>
	$D_0 \times 10^6$, mol/psia ^{0.5} -cm-min	$-\beta$, K	
Ackerman	3.85	794	0.619
Chabot	2.47	705	2.39
Serra	2.78	758	2.15
Smith	4.22	704	0.0586
Yoshida	1.92	690	3.92

¹Calculations based on values from Ackerman and Koskinas (1972), Chabot et al. (1988), Serra et al. (1998), current study, and Yoshida et al. (1981), respectively.

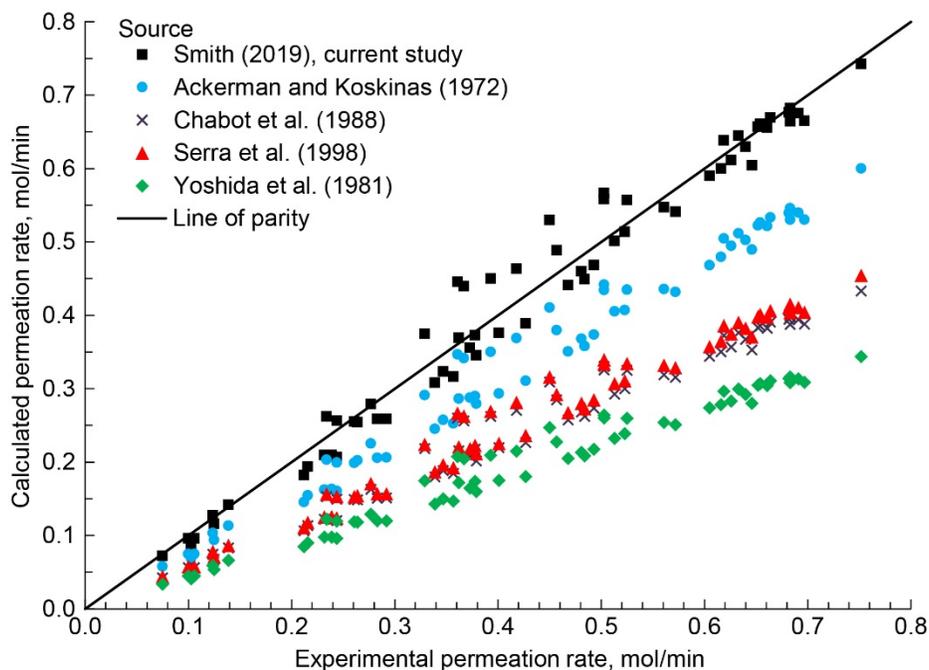


Figure 1.—Hydrogen permeation rates calculated with constants from various sources versus those experimentally determined.

For deuterium gas, the best-fit values for Equation (34) are shown in Table II along with the original Ackerman values and existing literature constants converted to equivalent units.

The constants determined in the current study (Smith) result in the best fit to the deuterium permeation experimental data. Again, all previously reported fit constants underestimate permeation rates compared with the experimental values. At near atmospheric pressures, it may be preferable to use the Serra constants, as those fit constants are based upon low-pressure operation. In Figure 2, the calculated permeation rates for deuterium are compared to the experimental permeation rates for each source of fitted constants.

TABLE II.—EMPIRICALLY DETERMINED CONSTANTS FOR EQUATION (34) WITH DEUTERIUM GAS AND RESIDUAL SUM OF SQUARES RELATIVE TO ACKERMAN EXPERIMENTAL DATASET

Source ¹	Fitted constants		Residual sum of squares, <i>RSS</i>
	$D_0 \times 10^6$, mol/psia ^{0.5} ·cm·min	$-\beta$, K	
Ackerman	1.68	479	0.127
Serra	1.71	740	0.520
Smith	2.12	468	0.0126
Yoshida	1.26	740	0.881

¹Calculations based on values from Ackerman and Koskinas (1972), Serra et al. (1998), current study, and Yoshida et al. (1981), respectively.

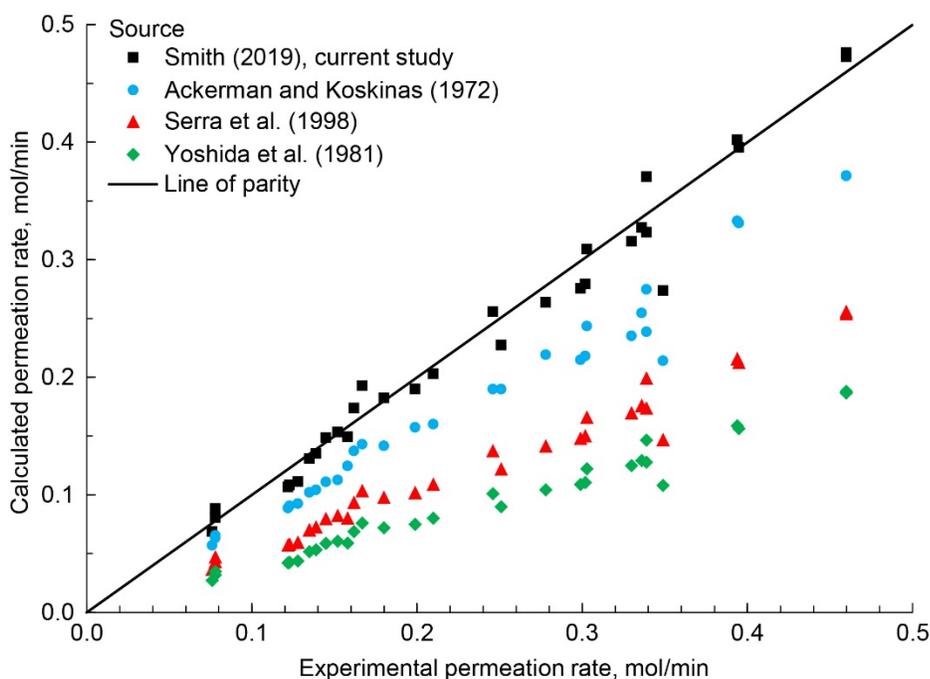


Figure 2.—Deuterium permeation rates calculated with constants from various sources versus those experimentally determined.

The amended Smith constants conform most closely to the line of parity for the entire temperature and pressure range. It is noteworthy that Serra and Yoshida independently produced a common β factor. Despite that temperature dependence relationship, all calculated permeation rates from the Yoshida constants generate a value less than the experimental value.

Conclusions and Recommendations

Using the original experimental data of Ackerman, the equation fits for hydrogen and deuterium permeation rates have been improved compared to other published values. This supports the applicability of the theoretical basis that includes Sieverts's law and the Arrhenius equation. A correlation was developed to model hydrogen and deuterium gas permeation over a wide range of temperatures and pressures. The fit of the predicted results to experimental permeation rate data was shown to be near linear. This is impressive, considering the measurement uncertainties noted in past publications and the limits of collected data.

For calculating pure hydrogen or deuterium permeation at greater than atmospheric pressure through Pd-25Ag, it is recommended to use the Smith constants presented here. Only in the case of deuterium supplied at lower pressures, near atmospheric, may it also be suitable to model the system with Serra constants. To improve data quality, future work should aim to improve temperature measurement capability and record measurements over a wide pressure range. Exceeding a supply pressure of 1,000 psi and a backpressure of 100 psi would stretch the range of this model equation.

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Appendix—Symbols

<i>A</i>	cross-sectional area
<i>C</i>	concentration of gas
<i>D</i>	diffusivity of gas
<i>D</i> ₀	factor in Equation (34)
<i>E</i> _{<i>A</i>}	activation energy
<i>f</i>	fugacity of gas
<i>G</i>	Gibbs free energy
<i>G</i> ⁰	Gibbs free energy at standard conditions
<i>H</i>	enthalpy
<i>J</i>	diffusion flux
<i>K</i>	equilibrium constant
<i>k</i>	Boltzmann constant
<i>N</i>	number of experimental trials
<i>N</i> _{<i>A</i>}	Avogadro constant
<i>n</i>	number of moles of gas
<i>P</i>	permeation rate
<i>p</i>	partial pressure of gas
<i>Q</i>	heat
<i>R</i>	ideal gas constant
<i>RSS</i>	residual sum of squares
<i>S</i>	entropy
<i>T</i>	temperature
<i>t</i>	thickness of medium
<i>U</i>	internal energy
<i>V</i>	volume
<i>W</i>	work
<i>x</i>	diffusion length
β	factor in Equation (34), $\frac{\Delta G^0 - 2E_A N_A}{2R}$

Subscripts

<i>a,b</i>	positions
<i>B</i>	final position at end of diffusion path on the backpressure side of medium
<i>calc</i>	calculated
<i>exp</i>	experimental
<i>m</i>	molar
<i>product</i>	product
<i>reactant</i>	reactant
<i>S</i>	initial position of diffusion path on supply pressure side of medium

