Modelling of hydrogen permeability of membranes for high-purity hydrogen production

Yury V Zaika and Natalia I Rodchenkova
Institute of Applied Mathematical Research, Karelian Research Centre, Russian Academy of Sciences, Pushkinskaya Street 11, Petrozavodsk, Russia
E-mail: zaika@krc.karelia.ru, nirodchenkova@krc.karelia.ru

Abstract. High-purity hydrogen is required for clean energy and a variety of chemical technology processes. Different alloys, which may be well-suited for use in gas-separation plants, were investigated by measuring specific hydrogen permeability. One had to estimate the parameters of diffusion and sorption to numerically model the different scenarios and experimental conditions of the material usage (including extreme ones), and identify the limiting factors. This paper presents a nonlinear mathematical model taking into account the dynamics of sorption-desorption processes and reversible capture of diffusing hydrogen by inhomogeneity of the material’s structure, and also modification of the model when the transport rate is high. The results of numerical modelling allow to obtain information about output data sensitivity with respect to variations of the material’s hydrogen permeability parameters. Furthermore, it is possible to analyze the dynamics of concentrations and fluxes that cannot be measured directly. Experimental data for Ta77Nb23 and V85Ni15 alloys were used to test the model. This work is supported by the Russian Foundation for Basic Research (Project No. 15-01-00744).

1. Introduction
The interest in the interaction of hydrogen isotopes with structural materials is multifarious [1–3]. It is sufficient to mention problems in power production, protection of metals from hydrogen corrosion, chemical reactor design, rocket production. Hydrides are able to retain large quantities of hydrogen. Hence, high expectations are attached to hydrogen batteries that avoid using ultra-high pressures or low temperatures. Plastification and thermo-hydrogen treatment of titanium alloys are based on reversible alloying of metals by hydrogen. Some particular problems of the hydrogen materials science connected with this article are investigated in [4,5]. Enthusiasts have been speaking about hydrogen economy along with hydrogen energy [3].

Experimental results show that physical-chemical phenomena at the surface are limiting factors [1, 2] along with the diffusion processes inside the metal. Transport parameters also depend on the specific technology of the material manufacturing. Therefore, it is not reasonable to target at ‘tabular data’. Instead, effective algorithms for processing experimental curves are necessary. The proposed mathematical model matches the experimental method of hydrogen permeability and takes into account only the main limiting factors and informative capabilities of the experiment. This mathematical research is based on the data on the hydrogen permeability of some promising alloys [6–8]. The experimental technique from [8] was employed.
2. Mathematical model

At first, we briefly describe the experiment. The material sample is a vacuum vessel barrier, pre-heated to a fixed temperature. Degassing of the sample was performed in advance. At the initial time instant the pressure of molecular hydrogen is built up by frequency jumping at the inlet. The declining pressure in the input chamber and increasing hydrogen pressure in the output chamber are measured. The informative capabilities of the experiment are limited, therefore, in the model we shall take into account only the main factors for the filtering problem.

Consider hydrogen transfer through the sample ($\ell$ is the plate thickness and $S$ is its area). The sample temperature $T$ is constant within a single experiment. The concentration of dissolved hydrogen (in the monatomic state) is sufficiently low and the diffusion flux can be considered proportional to the concentration gradient. Some of H atoms interact with traps. The traps are micro-defects of different nature including, for instance, micro-cavities, which can capture hydrogen. The equations taken as the diffusion model with limited capture within the plate are

$$\frac{\partial c}{\partial t} = D(T) \frac{\partial^2 c}{\partial x^2} - f(T, z, c), \quad \frac{\partial z}{\partial t} = f(T, z, c),$$

where $c(t, x)$ is the concentration of diffusing (atomic) hydrogen; $z(t, x)$ is the concentration of the captured diffusant; $D$ is the diffusion coefficient ($[D] = \text{cm}^2/\text{s}$); $a := a_{\text{in}}$ and $a_{\text{out}}$ are the coefficients of absorption and release of H atoms by traps. Sign $:= is used in the sense of equality by definition. The magnitude $z_{\text{max}} = \max z$ is considered to be sufficiently small (a metal alloy with high hydrogen permeability is investigated), so the capture is at the correction level and more detailed modelling of the capture process is not necessary. The summand $a_{\text{out}} z$ is negligible within the operating temperature range $T \in [400, 900] \text{K}$. On the scale of the establishment of the stationary permeability mode for relatively thin membranes the traps quickly become saturated and have practically no effect on the penetrating flux. Therefore, hereinafter we suppose that $a_{\text{out}} = 0$. This coefficient is significant in the ‘saturation-degassing’ experiment at high temperatures, and setting of the value at $a_{\text{out}} > 0$ technically does not complicate the numerical solution of the initial boundary-value problem. Coefficients $D, a$ depend on the sample temperature $T$ in an Arrhenius way with pre-exponential factors $D_0, a_0$ and activation energies $E_D, E_a (R - \text{absolute gas constant})$: $D = D_0 \exp\{-E_D/\{RT(t)\}\}$, $a = a_0 \exp\{-E_a/\{RT(t)\}\}$. Initial data are determined by the fact that the sample had been preliminarily degassed $c(0, x) = 0$, $z(0, x) = 0$.

Nonlinear boundary conditions are derived from the material flux balance:

$$- \frac{dQ_{\text{in}}}{dt} = \left[\mu(T)s(T)p_0(t) - b(T)c^2_0(t)\right] S = -SD \frac{\partial c}{\partial x}|_{x=0},$$

$$- \frac{dQ_{\text{out}}}{dt} = \left[\mu(T)s(T)p_\ell(t) - b(T)c^2_\ell(t)\right] S = SD \frac{\partial c}{\partial x}|_{x=\ell}.$$  

Here, $Q_{\text{in}}(t), Q_{\text{out}}(t)$ are the amounts of hydrogen atoms in the input chamber of volume $V_{\text{in}}$ and output chamber of volume $V_{\text{out}}$, $c_0(t) := c(t, 0)$, $c_\ell(t) := c(t, \ell)$. The gaseous hydrogen is in molecular form, but for consistency (atomic hydrogen diffuses through the metal) we use atoms as the unit of amount. According to the gas kinetic theory, the incident particle flux density $J_p$ is connected with the pressure $p$ by the Hertz–Knudsen formula: $J_p = p/\sqrt{2\pi mkT}$ ($k$ is the Boltzmann constant, $m$ is the mass of a hydrogen molecule). In the context of the experiment it is convenient to select the following units $[\ell] = \text{cm}$, $[p] = \text{Tor}$. Then we numerically obtain the dependence $J_p = \mu p$, $\mu(T) \approx 2.474 \cdot 10^{22}/\sqrt{T}$ ($[\mu] = 1_{\text{H}_2}/(\text{Tor cm}^2 \text{s})$, $[T] = \text{K}$, the numerical value of $T$ is under the root sign). Only a small part of ‘incident’ H atoms will however be
absorbed into the membrane volume. This fact is reflected by the multiplier \( s \). Thus, \( \mu sp \) is the resulting flux of atoms through the surface into the bulk without differentiation into more elementary stages (adsorption, chemosorption, dissociation, dissolution). One can write \( 2s \) instead of \( s \) and interpret \( s \) as the fraction of absorbed H atoms.

Hereinafter, \( J_{0,i} = b c_{0,i}^2 \) are the densities of the desorption flux from the sample (deviation from the square desorption law is significant only at extreme temperatures), \( b \) is the desorption coefficient ([\( b \]) = \( \text{cm}^3/\text{s} \)). We will usually omit the word density assuming that the surface has unit area. We suppose that coefficients \( s \) and \( b \) also depend on the temperature in an Arrhenius way. Formally, one can write the Arrhenius dependence for \( s \), but in the exponent the ‘activation energy’ \( E_s \) may also be negative as a linear combination of the activation energies and heats of surface processes on the way ‘from gas to the solution’. If the saturation pressure \( \bar{p} \) on both sides of the membrane is constant at \( T = \text{const} \), then the equilibrium concentration \( \bar{c} \) of dissolved atomic diffusive hydrogen is eventually established. From the model (2), (3), when all derivatives are zero, we have \( \bar{c} \propto \sqrt{\bar{p}} \): \( \bar{c} = \Gamma \sqrt{\bar{p}} \), \( \Gamma := \sqrt{\mu s/b} \). Therefore, the model is consistent with the Sieverts’ law adequacy range (\( \bar{c} \propto \sqrt{\bar{p}} \))

The range \([p_{\text{min}}, p_{\text{max}}]\) is narrow, so we restrict ourselves to the relation \( z_{\text{max}} = \sigma \bar{c} \), \( \sigma \leq 0.1 \). This restriction will not lead to failure of the Sieverts’ law (\( \bar{c} + z_{\text{max}} \propto \sqrt{\bar{p}} \)) while \( \bar{c} + z_{\text{max}} \approx \bar{c} = \Gamma \sqrt{\bar{p}} \) is within the experimental accuracy range. It now remains to find the magnitudes of \( Q_{\text{in}}, Q_{\text{out}} \). Within the transfer time the gas is in the thermodynamical quasi-equilibrium with the surface, therefore we use the formula \( N = pV/(kT) \). Here, \( N \) is the number of gas particles occupying the volume \( V \) at the temperature \( T = T_v \) and the pressure \( p \) (in the SI system \([p] = \text{Pa}, [V] = \text{m}^3, [k] = \text{J/K}) \). Taking into account the relationships Torr = 133.322 Pa, Pa = J/m\(^3\) (formally), we get the following expressions for the corresponding pressures and volumes in the boundary conditions (2), (3) \( Q = 2N = \alpha pV/T, \alpha \approx 1.931 \cdot 10^{19} \). Here, \( p, V, T \)

are the numerical values of variables in the selected units (Torr, cm\(^3\), K).

Formally, zero initial conditions and the boundary condition \((x = 0)\) of the flux balance are inconsistent at \( t \to +0 \). In fact, ‘instant’ hydrogen input lasts for some, even if negligibly short, time. This fact has been taken into account in the solution algorithm of the initial boundary-value problem, which is omitted here. Mathematically, without reference to the computational algorithm, we should talk about the problem in terms of the theory of generalized solutions.

### 3. Results of numerical modelling

The input data are \( T = 400^\circ \text{C}, \ell = 0.014 \text{cm}, S = 0.785 \text{cm}^2, V_{\text{in}} = 3000 \text{cm}^3, V_{\text{out}} = 1750 \text{cm}^3 \). The result of approximation of experimental data for the Ta\(_{77}\)Nb\(_{23}\) alloy [8, Fig. 1] by the model curves (inlet and outlet pressures of molecular hydrogen) is shown in Fig. 1. We comment on Fig. 2. According to the accepted model, the equilibrium concentration \( \bar{c} \) under saturation conditions \( p = \text{const} \), \( T = \text{const} \) is determined (when all derivatives are zero) as \( \bar{c} = \Gamma \sqrt{\bar{p}} \), where \( \Gamma = \sqrt{\mu s/b} \) is the solubility coefficient. But we shall keep in mind that only dissolved atomic diffusive hydrogen is considered. Degassing is thought to be complete at the concentration \( \bar{c} + z_{\text{max}} = \Gamma \sqrt{\bar{p}} \). In the accepted model \( \Gamma_{\text{max}} = \Gamma [1 + \sigma] \), and the Sieverts’ law holds true \( \bar{c} + z_{\text{max}} \propto \sqrt{\bar{p}} \). In Fig. 2 with a hypothetical value \( z_{\text{max}} = 10 \bar{c} \) total solubility is fixed at an order of magnitude greater than in Fig. 1. If a steady-state flux of hydrogen permeability \( J = -D \partial_n c \) is registered in a breakthrough experiment where \( p_0(t) = p = \text{const} \) and vacuum is created at the outlet, we have \( J = \Phi \sqrt{\bar{p}}/\ell, \Phi := D\Gamma = D\sqrt{\mu s}/b \) on the assumptions that \( c_0 = \bar{c}_0 = \Gamma \sqrt{\bar{p}}, c_0 = 0 \). If within a set of experiments (\( T = \text{const}, p \) is varied) the proportionality \( J \propto \sqrt{\bar{p}} \) is registered with acceptable accuracy, then so-called hydrogen permeability coefficient \( \Phi \) is determined using the values of \( p, J \) (using only the formula \( J = \Phi \sqrt{\bar{p}}/\ell \), and disregarding information about the accepted model and the values of \( D, \Gamma \)). The permeability is determined by the diffusing hydrogen (in the model \( \Phi = D\Gamma \)). If the permeability \( \Phi \) is calculated from available independent values of the diffusion and solubility coefficients (derived from different experiments and with
Figure 1. Approximation of pressures, 400°C. Figure 2. Pressures in the case of $z_{\text{max}} = 10 \bar{c}$.

total solubility including captured hydrogen), then we can obtain $D\Gamma_{\text{max}} \gg D\Gamma$. Evidently, it is one of the main factors for the scatter in the data on the solubility and permeability coefficients. The problem is the following: for thin membranes in the permeability mode it is difficult to detect the loss of hydrogen captured by traps even if the traps’ capacity is high and it essentially influences the total solubility inside the material.

Let us proceed to the analysis of the bulk concentration dynamics during the ‘communicating vessels’ experiment. We begin with near-to-surface concentrations ($x = 0, \ell$) – Figs. 3, 4. The traps became saturated during one minute: $z_0 \approx z_\ell \approx z_{\text{max}}$. The concentrations $c_0(t) = c(t, 0)$, $c_\ell(t) = c(t, \ell)$ quickly get stabilized, but one can see this curve’s behavior is local on two-hour scale: the transient regime of splash is changed to a slow trend line. A comparable stabilization time $c_\ell$ (with respect to $c_0$) is due to the fast hydrogen permeability of the alloy and $\ell \ll 1$.

The high velocity of the transient process is predictable, since the characteristic diffusion time $\ell^2 / D$ ($D \sim 10^{-5}$) is within ten seconds. The total concentration is determined by the sum $c + z$. Quasi-equilibrium (Sieverts’) concentrations of diffusing hydrogen $c_{0,\ell} \propto \sqrt{p_0\ell}$ are determined using the molecular hydrogen pressure by the formulas $\mu sp_{0,\ell} = b c_{0,\ell}^2$; $c_{0,\ell}(t) = \Gamma \sqrt{p_0(t)}$. Considering hydrogen capture by traps we should use the sums $\bar{c}_{0,\ell}(t) + z_{\text{max}}$ and $c_{0,\ell}(t) + z_0(t)$.
Fig. 4 allows to estimate how much higher the difference of concentrations $c_\ell - \bar{c}_\ell$ at the outlet is compared to that at the inlet $c_0 - \bar{c}_0$. The difference of inlet/outlet concentration range will decline only asymptotically. In the context of the gas separation problem we are firstly interested in the penetrating flux. But the approximation of the gradient $\partial c$ by the difference quotient $(c_\ell(t) - c_0(t))/\ell$ suffers when we use quasi-equilibrium estimates at both the inlet ($\bar{c}_0 > c_0$) and the outlet ($\bar{c}_\ell < c_\ell$). The results for the V$_{85}$Ni$_{15}$ alloy are qualitatively similar.

4. Fast hydrogen permeability model

The Richardson approximation in a quasi stationary state (when the concentration distribution of diffusing hydrogen in the volume is linear)

$$J(t) = -D\partial_x c = DE^{-1}[c_0(t) - c_\ell(t)] \approx J_R(t) = D\Gamma \ell^{-1}\sqrt{p_0(t) - p(t)}$$

is usually used to analyze hydrogen permeability (see, for instance, [6, 8]). It is shown above that substitution of equilibrium concentrations leads to a significant error where the membrane is very thin and the alloy is chosen to achieve fast hydrogen permeability. We formulate the problem of modelling the concentrations $c_{0,\ell}$ using the pressures $p_{0,\ell}$ (the problem is also of interest per se) without quasi-equilibrium simplification $c(t) = \Gamma \sqrt{p(t)}$.

The quasi-stationary state is achieved within a time $t_0$, which is short compared to total experiment time (the traps become saturated and $\partial_x c = -[c_0(t) - c_\ell(t)]/\ell$):

$$\dot{p}_{0,\ell}(t) = \mp\beta_{0,\ell}[c_0(t) - c_\ell(t)], \quad \beta_{0,\ell} \equiv SD\left[\alpha V_{in,\ell} \ell^{-1} T_V\right],$$

$$\mu S p_{0,\ell}(t) - b c_{0,\ell}^2(t) = \pm D \ell^{-1}[c_0(t) - c_\ell(t)], \quad t \geq t_0 > 0.$$  

Since $\dot{p}_\ell(t) = -V_{in}^{-1} V_{out}^{-1} \dot{p}_0(t) \Rightarrow p_\ell(t) = p_\ell(t_0) + V_{in}^{-1} V_{out}^{-1}[p_0(t_0) - p_0(t)]$, it is sufficient to express $c_{0,\ell}(t) = c_{0,\ell} p_0(t)$ from the boundary conditions (5) and substitute them into the first equation of (4) (the sign depends on the order of the sequence $0, \ell$).

For numerical modelling it is convenient to introduce dimensionless variables

$$X_{0,\ell}(t) = 1 + 2c_{0,\ell}(t)bD^{-1}, \quad a_{0,\ell}(t) = 4\ell^2 \Gamma^2 p_{\ell,0}(t)b^2 D^{-2} - 1.$$  

In addition, the system of equations (5) is compactly written in the symmetric form $a_0 + 2X_\ell = X_\ell^2$, $a_\ell + 2X_0 = X_\ell^2$. For the variable $X \equiv X_\ell$ we get an equation $[X^2 - a_\ell]^2 = 4[2X + a_0]$, which can be solved in radicals (we are interested in the positive root). However, the explicit expression is cumbersome and we will anyway have to numerically integrate the first equation of (4) in the form $\dot{p}_0 = f(p_0)$. Therefore, we shall aim to derive differential equations for $X_{0,\ell}$, since information about the dynamics of boundary concentrations $c_{0,\ell}$ is also of interest per se.

Differentiate the equations (5) with respect to time and substitute the pressure derivatives from (4). In the variables $X_{0,\ell}$ we obtain the system ($\mu \propto 1/\sqrt{T}$):

$$\dot{X}_0(t) = -s M_0 (X_0 - X) \cdot \frac{X_\ell - V_{in}^{-1} V_{out}^{-1} X_0 X_\ell^{-1} - 1}{X_0 X_\ell^{-1} - 1}, \quad M_0 \equiv \frac{\mu S T_V}{\alpha V_{in}},$$

$$\dot{X}_\ell(t) = s M_\ell (X_0 - X) \cdot \frac{X_0 - V_{in}^{-1} V_{out}^{-1} X_0 X_\ell^{-1} - 1}{X_0 X_\ell^{-1} - 1}, \quad M_\ell \equiv \frac{\mu S T_V}{\alpha V_{out}}.$$  

Let us formulate step-by-step the numerical modelling algorithm for the current values of $D$, $b$, $s$ (the authors used the freeware Scilab-6). We target at the ‘normal’ experimental conditions [6–8], including the parameters $p$, $T$, $\ell$, $V$, $S$.

1. We fix $t = t_0$: fast transient processes are omitted (in the example above the duration of transient processes is about tens of seconds on an hours-long experimental time scale). For
the variable \( X \equiv X_\ell \) we numerically solve the incomplete biquadratic equation \( [X^2 - a_\ell(t_0)]^2 = 4(2X + a_0(t_0)) \). The mathematical package will naturally provide us with four roots, from which we choose the positive one for which \( X^2 - a_\ell > 2X \) because \( c_\ell < c_\ell \). From the equations system \( a_0 + 2X_\ell = X_\ell^0, a_\ell + 2X_0 = X_\ell^0 (t = t_0) \) we find the missing value \( X_0(t_0) \). Formally, one equation is enough, but we consider averaging procedures including determination of the values of \( p_{0,\ell}(t_0) \).

2. We numerically integrate the system (7), (8) \((t \geq t_0)\) with the obtained initial data. The precaution is the following: the data should be redefined as real, otherwise the ‘imaginary’ component of the concentration begins to accumulate.

3. The change of variables in (6) determines the concentrations \( c_{0,\ell}(t) \) from which the model pressures \( p_{0,\ell}(t), t \geq t_0 \), are calculated using the equations (5).

Computational experiments show that the model curves almost coincide \((t \geq t_0)\) with those generated by the original model, viz nonlinear distributed initial boundary-value problem. All the varying parameters \( D, b, s \) of the original model that influence permeability are essential when implementing the algorithm described above. Thus, the simplified fast hydrogen permeability model does not lose in informativeness concerning transport parameters.

Conclusions
The hydrogen permeability model is focused on the task of material selection for the membrane technology of high-purity hydrogen production. The physico-technical nature of the problem involves the assessment of the main integrated transport indices keeping in mind the limited experiment informativeness. In particular, the parameter of the maximum trap capacity \( z_{\text{max}} \) does not consider the variety of traps.

Iterative solution of the distributed nonlinear initial boundary-value problem for approximation of the experimental data (in order to estimate the transport parameters) requires application of specialized software. On the other hand, for thin membranes with fast hydrogen permeability the Richardson approximation (when the boundary concentrations of the dissolved hydrogen are considered as quasi-equilibrium and corresponding to the Sieverts’ law) only allows to evaluate the order of the permeability coefficient.

The paper presents a fast hydrogen permeability model in the form of a system of two ordinary differential equations, which is equivalent to the original initial boundary-value problem (excluding the initial transient process). It allows to quickly ‘scan’ the material within a wide range of parameters: after parametric identification based on limited experimental information the material’s operating conditions can be manipulated to include extreme ones. Of course, we are speaking here about mathematical modelling aimed to estimate the transport parameters.

References
[1] Alefeld G and Völk J (Eds) 1978 Hydrogen in Metals (Berlin; New York: Springer) vol I Basic Properties p 427, vol II Application-oriented Properties p 387
[2] Zakharov A P (Ed) 1987 Interactions of Hydrogen with Metals (Moscow: Nauka) p 296
[3] Ball M and Wietschel M (Eds) 2009 The hydrogen economy (Cambridge University Press) p 646
[4] Zaika Yu V and Bormatova E P 2011 Parametric identification of a hydrogen permeability model by delay times and conjugate equations Int. J. Hydrogen Energy 36 1295–1305
[5] Zaika Yu V and Rodchenkova N I 2013 Hydrogen-solid boundary-value problems with dynamical conditions on surface Math. Modelling (New York: Nova Sci. Publishers) 209–302
[6] Dolan M D 2010 Non-Pd BCC alloy membranes for hydrogen separation J. Membrane Science 362 12–28
[7] Song G, Dolan M D, Kellam M E, Liang D and Zambelli S 2011 V-Ni-Ti multi-phase alloy membranes for hydrogen purification J. Alloys and Compounds 509 9322–28
[8] Kozhakhmetov S, Sidorov N, Piven V, Sipatov I, Gabiš I and Arinov B 2015 Alloys based on Group 5 metals for hydrogen purification membranes J. Alloys and Compounds 645 S36–S40