Journal of Membrane Science 335 (2009) 51–57

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Hydrogen gas-driven permeation through the membrane with asymmetric surface conditions

A. Pisarev*

Moscow Engineering and Physics Institute, Kashirskoe Sh., 31, 115409 Moscow, Russian Federation

ARTICLE INFO

Article history:
Received 4 June 2007
Received in revised form 3 February 2009
Accepted 28 February 2009
Available online 14 March 2009

PACS:
66.10.Cb
66.30.−h
66.30.Jt

Keywords:
Hydrogen permeation
Metal membranes
Surface processes
Diffusion
Absorption
Desorption
Regimes of permeation

ABSTRACT

Permeation through the membrane with different surface conditions on the inlet and outlet sides is analyzed. Two regime parameters characterizing the rates of processes on two sides of the membrane with respect to the rate of bulk diffusion are introduced. These regime parameters determine the concentration profile and the permeation rate. General equations for the concentration and the permeation flux are obtained. Three basic limit regimes are considered as partial limit cases of the general equations. These are diffusion limited regime (DLR), outlet surface limited regime (OLR), and inlet surface limited regime (ILR). The latter has two modes with qualitatively different concentration profiles. Boundaries between the regimes and approximation formulas for the permeation rates in these regimes have been found. Features of permeation in the limit cases and in intermediate regions are analyzed.

1. Introduction

Hydrogen permeation through metal membranes has been investigated for about a century; and intensive experimental researches for various applications are accompanied by the theoretical analysis. Permeation through the metal membrane depends on both surface processes and bulk processes, and can be limited by one of them. The classical expression for the steady state permeation rate limited by diffusion was given by Richardson et al. many years ago [1], and still it is widely used both in the experiment and in practice. This expression is only valid if the surface processes of hydrogen absorption and desorption are very fast and do not retard permeation. Later, Wang [2] first analyzed the problem of permeation in conditions of influence of surface processes. He proposed the scheme of permeation, which is still also often used. The permeation process was considered to consist of the stages of dissociative chemisorption on the inlet surface, subsequent absorption under the surface, diffusion through the bulk of the membrane, transition from the bulk into the chemisorption states on the outlet surface, and, finally, recombinative desorption from chemisorption states into vacuum. Forward and backward through-the-surface transitions were considered both on the inlet and the outlet sides of the membrane. Later, Livshits [3,4] introduced intermediate just-under-the-surface sites between the adsorption site on the surface and the interstitial sites deeper in the bulk. The scheme of Wang and its later modifications incorporate many parameters, which are often unknown from the experiment. Therefore, Ali-Khan et al. [5] simplified the consideration of the surface processes. Suggesting that the exchange processes between on-surface adsorption states and under-surface absorption states in the Wang model are very fast, it was suggested that the on-surface concentration and the under-surface bulk concentration are always proportional. Therefore, the desorption rate was written to be proportional to the squared bulk concentration with the proportionality coefficient being the product of the recombination coefficient and the surface roughness. Several attempts have been made to calculate the recombination coefficient. Particularly, Baskes [6], Pick and Sonnenberg [7], and Richards [8] considered various channels of recombination in obtaining their expressions for the recombination coefficient that were analyzed by Pisarev and Ogorodnikova [9]. As permeation is a complex process, which depends on surface and bulk effects, Ali-Khan et al. [5] and Notkin [10] analyzed the interplay between bulk diffusion and surface effects and demonstrated various regimes of permeation. Ali-Khan introduced the terms the

---

* Tel.: +7 495 3239325.
E-mail address: pisarev@plasma.mephi.ru.

0376-7388/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.memsci.2009.02.041

diffusion limited regime (DLR) of permeation and the surface limited regime (SLR) of permeation. Though, Wang and Ali-Khan et al. permitted the surface conditions to be different on the two sides of the membrane in general, the analyses was only made for symmetric membranes. This was the case the inlet and the outlet surfaces had the same characteristics. Andrew and Haasz [11] analyzed possible blocking of permeation if the surface coverage became close to 1. The membrane was also considered to be symmetric. At the same time, in many cases the surface conditions are not identical on the inlet and outlet surfaces. Livshits [4] first analyzed the situation of asymmetric conditions on the two sides of the membrane and demonstrated specific effects in permeation connected with this asymmetry. Unfortunately, the desorption rate was written to be of the first order, which is not the case of molecular gases in usual conditions. Besides, hydrogen mass transport in the solid bulk was modeled by the ideal gas equations, but not by the diffusion task. Later, permeation through membranes with different conditions on two surfaces in SLR was considered by Waelbroeck et al. [12] and by Pisarev et al. in [13,14] using the Ali-Khan approach for surface processes. Pisarev and Bacherov [15] have also performed a comparison between numerical calculations and analytical formulas for dynamics of permeation in DLR and SLR for asymmetric surface conditions and have found boundaries for analytical solutions.

This paper gives general equations for the steady state permeation rate and concentration through the asymmetric membrane and analyses the interplay of bulk and surface processes in permeation through the membrane with asymmetric surfaces. The consideration takes into account diffusion, dissociative absorption, and recombinative desorption.

2. Model

Let us consider a membrane of the thickness L made of material with the diffusion coefficient D and solubility S, which separates two volumes: one with hydrogen under the pressure p and another one under vacuum.

If the absorption coefficient of hydrogen molecules on the inlet side is α_1, the absorption flux on the inlet side can be written as

$$i_{\text{abs}} = 2\alpha_1 p \text{ atoms/(cm}^2\text{ s)},$$

Let us follow [5] in writing the desorption flux as the product of the squared bulk concentration u, the recombination coefficient k, and the surface roughness σ. Let us also introduce the effective recombination coefficients $K_1 = \sigma_1 k_1$ and $K_2 = \sigma_2 k_2$ on the inlet and outlet sides, respectively. Let us denote the steady state bulk concentrations on the inlet and outlet sides as u_1 and u_2, respectively. The desorption fluxes from the inlet and outlet sides can be written then as

$$j_1 = K_1 u_1^2 \text{ atoms/(cm}^2\text{ s)}$$

$$j_2 = K_2 u_2^2 \text{ atoms/(cm}^2\text{ s)}.$$

With these denotations, one can write two equations that give balances of particle fluxes in the steady state:

$$2\alpha_1 p = K_1 u_1^2 + K_2 u_2^2, \tag{1}$$

$$\frac{D(u_1 - u_2)}{L} = K_2 u_2^2. \tag{2}$$

The first equation is the net balance of fluxes in the membrane. The second equation is the balance of fluxes on the outlet side of the membrane.

There are three parameters in Eq. (1) α_1, K_1, K_2, but only two of them are free. One can link the absorption and recombination coefficients. This can be done if to consider a solid sample embedded in gas, which is the case of experiments on solubility. The absorption flux and recombination flux are equal in equilibrium:

$$2\alpha p = K c_s^2.$$

This equation can be re-written as

$$c_s = S p^{1/2}. \tag{3}$$

with

$$S^2 = \frac{2\alpha}{K} \tag{4}$$

Expression (3) is well known as the Sieverts law, where S is the solubility that determines the equilibrium concentration c_s in solid at a given pressure p. The solubility is a basic characteristic of solid, and therefore it can be considered as an experimentally known one. Relation (4) is valid both for the inlet and outlet sides.

Eqs. (1) and (2) can be re-written in a dimensionless form using the following dimensionless parameters.

$$U_1 = \frac{u_1}{c_s},$$

$$U_2 = \frac{u_2}{c_s},$$

$$W_1 = \frac{K_1 L c_s}{D} = 2\alpha_1 L\, p^{1/2} S^{-1} D^{-1},$$

$$W_2 = \frac{K_2 L c_s}{D} = K_2 L\, p^{1/2} S D^{-1},$$

$$\gamma = \frac{K_2}{K_1} = \frac{W_2}{W_1}.$$

Here U_1 and U_2 stand for the concentrations on the inlet and outlet sides normalized to the Sieverts concentration at a given solubility and hydrogen pressure. Parameters W_1 and W_2 are the parameters that characterize the relative rates of diffusion and surface processes. The relative rates of absorption and diffusion are of interest on the inlet side, while the relative rates of desorption and diffusion are of interest on the outlet side. Parameter W was introduced earlier in [5] for the symmetric membrane and has the names “the transport parameter” and “the permeation number”. The last parameter γ characterizes the asymmetry of surface properties of the membrane; so we name it as the asymmetry parameter.

Having these parameters in hands, one can re-write Eqs. (1) and (2) as

$$U_1^2 + \gamma U_2^2 = 1. \tag{5}$$

$$U_1 = W_2 U_2^2 + U_2 \tag{6}$$

Combining (5) and (6), we come to the following equation with respect to U_2.

$$W_2^2 U_2^4 + 2W_2 U_2^3 + (1+\gamma) U_2^2 = 1 \tag{7}$$

If the two surfaces of the membrane are identical, in other words, the membrane is symmetric ($W_1 = W_2 = W$), Eq. (7) is reduced to the equation obtained in [5]:

$$W^2 U_2^4 + 2W U_2^3 + 2U_2^2 = 1.$$

The concentrations on the two sides of the symmetric membrane are linked by $U_1^2 + U_2^2 = 1$.

As the rate of permeation is given by

$$j = K_2 u_2^2 \text{ atoms/(cm}^2\text{ s)},$$