Journal of Membrane Science 394–395 (2012) 131–139

Contents lists available at SciVerse ScienceDirect

Journal of Membrane Science

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

Assessing the coupled heat and mass transport of hydrogen through a palladium membrane

Ragnhild Skorpa[a], Mari Voldsund[a], Marit Takla[a], Sondre K. Schnell[b], Dick Bedeaux[a], Signe Kjelstrup[a,b,*]

[a] *Department of Chemistry, Faculty of Natural Science and Technology, Norwegian University of Science and Technology, Trondheim, Norway*
[b] *Process & Energy Laboratory, Delft University of Technology, Leeghwaterstraat 44, 2628CA Delft, The Netherlands*

ARTICLE INFO

Article history:
Received 30 August 2011
Received in revised form 6 December 2011
Accepted 23 December 2011
Available online 2 January 2012

Keywords:
Non-equilibrium thermodynamics
Soret effect
Membrane transfer coefficients
Dissociative adsorption

ABSTRACT

We have formulated the coupled transport of heat and hydrogen through a palladium membrane, including the dissociative adsorption of hydrogen at the surface. This was done using the systematic approach of non-equilibrium thermodynamics. We show how this approach, which deviates from Sieverts' law, makes is possible to calculate the direct impact that a temperature gradient, or a heat flux, has on the hydrogen flux. *Vice versa*, we show how the dissociative adsorption leads to heat sinks and sources at the surface.

Using a set of transport coefficients estimated from experimental values available in the literature, calculations were performed. An enhancement of the hydrogen flux through the membrane with 10% and 25%, by transmembrane temperature differences of 24.8 K and 65.6 K, respectively, was predicted with a feed temperature of 673 K. Similarly, a transmembrane temperature difference of −176.5 K was observed to stop the hydrogen flux (Soret equilibrium). The calculations are done with estimated transport properties for the surfaces. The results show that an effort should be put into determination of these. Such experiments are discussed.

1. Introduction

With increasing energy prices, and a limited supply of oil, it is of importance to improve the efficiency of the most common industrial processes. In this situation, membrane reactors are interesting. In a membrane reactor, a chemical reaction and the separation of resulting products can be performed in one process step. The products are removed continuously along the reactor. This *in situ* removal of the products (or of unwanted by-products from the chemical reaction), as well as the possibility of a high yield from equilibrium limited reactions, makes this a very interesting alternative to traditional reactors.

Membrane reactors can be put into two categories: porous and dense. Porous membranes can be *e.g.* zeolite-based membranes [1,2], while the palladium membrane is a typical example of a dense membrane. In industrial applications, there are several situations where one wishes to extract hydrogen from a reaction; the water–gas-shift reaction [3] is one of the most important. For other examples, see Basile [4]. The palladium membrane is a thin layer of palladium, often on a porous support of either steel or alumina. For a recent review of state of the art palladium membrane reactors, see Yun and Oyama [5]. Palladium is purely selective towards transport of H_2. In order to give a high flux of hydrogen through the membrane, the palladium-layer should be as thin as possible; typically a few micro meter or less. In a palladium reactor hydrogen is transported as hydrogen atoms in the palladium, and as hydrogen molecules in the gas phases on each side of the membrane [5,6]. The heat of adsorption is significant ($-87\,\mathrm{kJ\,mol^{-1}}$ [7]), including the splitting of molecular hydrogen and adsorption at the surface. This dissociative adsorption is likely to influence the mass flux. There is a need to study this in a systematic manner for several reasons. It is known that surface effects can hamper experiments [8]. Also, permeability studies often show deviation from Sieverts' law [9]. Furthermore, while it is known how the absolute temperature affects a chemical reaction, little is known on how a temperature gradient affects the reaction rate. With a thin membrane and large heat sinks and sources at the interfaces, such gradients may be large. The coupling of chemical reactions to fluxes of heat and mass is possible in principle [10], but has not been described in detail for a real system before.

In their now seminal paper, Ward and Dao [11], presented a model for hydrogen permeation through a palladium membrane which accounted for all kinetic steps in the permeation and reaction process. This model has been modified and improved to also include mass transfer through the support by others, and has been

---

* Corresponding author at: Department of Chemistry, Faculty of Natural Science and Technology, Norwegian University of Science and Technology, Trondheim, Norway. Tel.: +47 73594179.
E-mail addresses: signe.kjelstrup@chem.ntnu.no, signe.kjelstrup@nt.ntnu.no (S. Kjelstrup).

0376-7388/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.memsci.2011.12.033

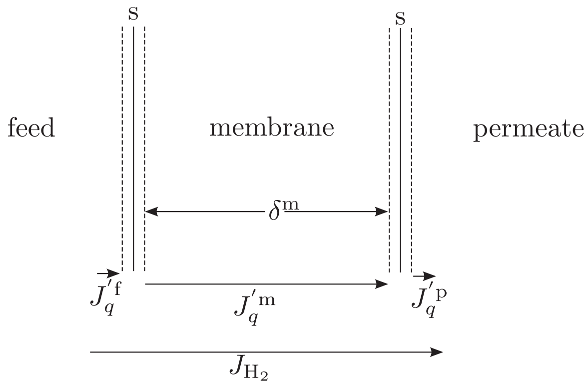

Fig. 1. A schematic illustration of the system. A palladium membrane of thickness δ^m is bounded by two planar surfaces of molecular thickness. The planes have no extension in the direction of transport on the scale used. The mass flux, J_{H_2}, is constant at stationary state, while the measurable heat flux, J_q', depends on the position in the system.

further used a basis for incorporating the surface and a reaction in reactor models [12–16]. Many of the existing models for hydrogen permeation neglects the effect of the surface, see *e.g.* [17,18]. None of these works deal with transport of heat in combination with transport of mass across surfaces.

This gives us a motivation to apply non-equilibrium thermodynamics to study the transport in a palladium membrane. The work of de Groot and Mazur [19] outlines how to describe homogeneous systems. During the last decade, the field has been further developed to also include heterogeneous systems, such as systems with membranes [20]. In the extension, dynamic boundary conditions for the crossing from one layer to the next were defined. The coupling, or the interaction of fluxes and forces at the surface, is often overlooked in the literature, while it is now known that it can be substantial [21]. It is, however, relevant to ask whether linear force–flux relations apply when a chemical reaction takes place in the system. Chemical reactions have normally rates which are nonlinear functions of their driving force, meaning that we then need to go to a mesoscopic level of description to capture this property [10]. In the present case, we shall see that there is no need to invoke this level of complication for operating conditions that are typical for palladium transport.

After a short description of the system and the system conditions used in Section 2, we proceed in Section 3 to derive transport equations, using non-equilibrium thermodynamics, across a palladium membrane. Details concerning the calculations and solution procedures are given in Section 4. In Section 5 we present and discuss the results obtained from applying the model to different sets of boundary conditions. We study in particular the effect the surface has on the transport across the membrane. In Section 6, we draw conclusions.

2. The system

Consider a palladium membrane separating two gas phases. For simplicity, we assume pure H_2 gas on each side. Hydrogen is transported from gas phase to gas phase, and the transport is considered to be 1-dimensional, in the direction perpendicular to the membrane. The membrane is considered to be a homogeneous system with thickness δ^{m}. The region between the gas phase and the palladium defines the membrane *surface*. There are two such planar layers of molecular thickness; one at each side of the membrane. The surface in equilibrium was described already by Gibbs as a two-dimensional system using excess thermodynamic properties. The same terminology is adopted here, following Kjelstrup and Bedeaux [20] for surfaces outside equilibrium. Fig. 1 illustrates the system with the different phases and with fluxes entering and leaving the system. Superscript s is used to denote the surface, while f and p stands for the feed- and the permeate sides, respectively. We shall not model the diffusion layers in the gas phase external to the surfaces. These layers might well be diffusion limiting, but this will not be addressed in the present paper.

Prior to membrane transport, hydrogen is adsorbed at the surface. The dissociative adsorption can be written as:

$$H_2(g) \rightleftharpoons 2H(ads). \tag{I}$$

The Gibbs energy difference, ΔG, for the dissociative adsorption at the feed side can then be defined as

$$\Delta G = 2\mu_{\mathrm{H}}^{\mathrm{m}} - \mu_{\mathrm{H}_2}^{\mathrm{f}}, \tag{1}$$

where μ_j^{i} is the chemical potential of component j in phase i evaluated close to the surface (here surface at the feed side). As only equations for the feed side of the membrane are given in detail in this paper, the superscripts indicating the phase (f, m or p) have been dropped for ΔG throughout the paper. For the permeate side, a similar expression as given in Eq. (1) can be obtained.

We shall study the stationary state, where there is no accumulation of mass anywhere in the system, and

$$r^s = \frac{1}{2}J_{\mathrm{H}} = J_{\mathrm{H}_2}. \tag{2}$$

Here r^s is the rate of the dissociative adsorption, J_{H} is the flux of atomic hydrogen through the membrane, and J_{H_2} is the rate of which H_2 enters and leaves the system per m^2.

The total heat flux, J_q, through the system is also constant in the stationary state, giving

$$J_q = J_q'^{\mathrm{f}} + J_{\mathrm{H}_2}H_{\mathrm{H}_2}^{\mathrm{f}} = J_q'^{\mathrm{m}} + J_{\mathrm{H}}H_{\mathrm{H}}^{\mathrm{m}} = J_q'^{\mathrm{p}} + J_{\mathrm{H}_2}H_{\mathrm{H}_2}^{\mathrm{p}}, \tag{3}$$

which rearranged gives

$$J_q'^{\mathrm{f}} = J_q'^{\mathrm{m}} + \Delta H J_{\mathrm{H}_2} = J_q'^{\mathrm{p}}, \tag{4}$$

where H_j^{i} is the enthalpy of component j in phase i, $\Delta H = 2H_{\mathrm{H}}^{\mathrm{m}} - H_{\mathrm{H}_2}^{\mathrm{f}} = 2H_{\mathrm{H}}^{\mathrm{m}} - H_{\mathrm{H}_2}^{\mathrm{p}}$ is the heat of dissociative adsorption and $J_q'^{\mathrm{i}}$ is the measurable heat flux in phase i. Constant enthalpy in each phase was assumed.

3. A thermodynamic description of transport

In Sections 3.1 (for the membrane) and 3.2 (for the surface) we present the entropy production for each subsystem. The entropy production determines the relevant forces and fluxes, and their interactions. For details in the derivation we refer to the literature [20]. All the presented equations are given for the feed side of the membrane and for the surface at the feed side only. Equations for the permeate side are analogous and can be found in a similar manner. The force–flux relationships defines the necessary and sufficient experiments for determining transport coefficients. We shall further make a link to the experimental data we take from the literature.

3.1. The membrane

The general expression for entropy production in a homogeneous phase is defined as the product sum of fluxes and forces, and is described in several texts on non-equilibrium thermodynamics, see *e.g.* [20,19]. For transport of heat and atomic hydrogen in the membrane, we have the following expression, choosing the representation with the measurable heat flux, $J_q'^{\mathrm{m}}$

$$\sigma^{\mathrm{m}} = J_q'^{\mathrm{m}}\frac{\partial}{\partial x}\left(\frac{1}{T}\right) + J_{\mathrm{H}}^{\mathrm{m}}\left(-\frac{1}{T^{\mathrm{m}}}\frac{\partial \mu_{\mathrm{H},T}}{\partial x}\right). \tag{5}$$