GAS TRANSPORT IN INORGANIC MEMBRANES

VITTORIO BOFFA

MOLECULES@SURFACES

BARDONECCHIA – WINTER SCHOOL 2016
Outline

• Definition of membranes and their applications;
• Membrane properties;
• Gas-transport in multi-layer inorganic membranes;
• Methods for membrane fabrication.
What is a membrane?

A membrane is defined by IUPAC as a structure, having lateral dimension much greater than its thickness, through which mass transfer occurs under a variety of driving forces.*

This is the most general definition of membrane. However, this definition does not include the main function of a membrane:

Membranes are fabricated for separating molecules, ions or colloids. Membrane processes are characterized by the fact that the feed flow is divided in two streams called permeate (what passes through the membrane) and retentate (what doesn’t pass through the membrane).

Reverse Osmosis is an example of membrane process.

Microporous silica membranes

Feed

Membrane

Permeate

Membrane module

Asymmetric multilayer membrane structure

Permeate side

selective layer

retentate side

C₃H₈

CH₄

N₂

H₂S

CO₂

H₂

H₂O

4.3

3.8

2.65 Å
Upcoming technology platforms for green fuel production require the development of advanced molecular separation processes for recovering liquid biofuels, biomethane and hydrogen.

Gas separation

- H₂ purification
- CO₂ sequestration
- Biogas upgrading

Pervaporation

- Alcohol dehydration
- Separation of organic solvents

BARDONECCHIA 2016, MOLECULES @ SURFACES
Microporous
Pore diameter = 2 nm

Mesoporous
2 nm < D_p < 50 nm

Macroporous
Pore diameter > 50 nm

Architecture
• Thin active layer
• High permeability
Membrane properties

Flux and permeance

The efficiency of membranes is generally described in terms of permeance and selectivity.

Permeance (F)

\[ F_a = \frac{J_a}{\Delta P_a} \]

\( J_a \) = flux of the species “a” across the membrane

\( \Delta P_a \) = is the difference in partial pressure of “a” between the two sides of the membrane.

Permeability (\( \overline{F} \)) allows comparing membrane materials.

\[ \overline{F}_a = F_a \cdot L \]

L = membrane thickness

Selectivity and ideal selectivity

Selectivity is quantitatively expressed by the separation factor (\( \alpha \)):

\[ \alpha = \frac{x_{\text{retentate}}}{y_{\text{retentate}}} \cdot \frac{y_{\text{permeate}}}{x_{\text{permeate}}} \]

In the case of a gaseous mixtures, \( x \) and \( y \) are the partial pressures of the two components \( X \) and \( Y \).

ideal selectivity or permselectivity.

\[ F_{a/b} = \frac{F_a}{F_b} \]
Exercise 1a.:

- Membrane 1 is a microporous silica membrane supported on a highly porous ceramic support. The resistance to the gas flux of this support is negligible compared to the one of the silica layer. The silica layer is 250 nm thick. The trans-membrane hydrogen molar flux at 200 °C and \( \Delta P = 4 \text{ bar} \) \( (4 \cdot 10^5 \text{ Pa}) \) is 0.4 mol s\(^{-1}\) m\(^{-2}\). Calculate the membrane permeance.

\[
F_a = \frac{J_a}{\Delta P_a}
\]

\[
F_{\text{H}_2} = 0.4 \text{ (mol s}^{-1} \text{ m}^{-2}) / 4 \cdot 10^5 \text{ Pa} = 1 \cdot 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}
\]

\[
J_a = [\text{mol m}^{-2} \text{ s}^{-1}], \quad \Delta P_a = [\text{Pa}], \quad F_a = [\text{mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}]
\]
Membrane 1 has thickness of 250 nm and H₂ permeance of $1 \cdot 10^{-6}$ mol m⁻² s⁻¹ Pa⁻¹

Membrane 2 consists of a microporous amorphous carbon layer supported on a porous metallic tube, which has a filtering area of about 0.02 m² (319 mm long and has inner diameter of 20 mm). The resistance to the gas flow of this support is negligible compared to the one of the microporous carbon layer, which is 2.0 μm thick. The hydrogen molar flow rate at $\Delta P = 2.0 \cdot 10^5$ Pa and 200 °C was measured to be $1.0 \cdot 10^{-3}$ mol s⁻¹. Calculate the membrane permeance.

$$F_{H2} = 1.0 \cdot 10^{-3} \text{ (mol s}^{-1}) / [2.0 \cdot 10^5 \text{ Pa} \times 0.02 \text{ m}^2] = 2.5 \cdot 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$$

Which of the two membrane materials has the highest hydrogen permeability ($\overline{F}$) at 200 °C?

$$\overline{F}_{H2, \text{membr. material 1}} = 1 \cdot 10^{-6} \text{ (mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}) \times 2.5 \cdot 10^{-7} \text{ m} = 2.5 \cdot 10^{-13} \text{ mol m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$$

$$\overline{F}_{H2, \text{membr. material 2}} = 2.5 \cdot 10^{-7} \text{ (mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}) \times 2 \cdot 10^{-6} \text{ m} = 5.0 \cdot 10^{-13} \text{ mol m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$$

$$J_a = [\text{mol m}^{-2} \text{ s}^{-1}] \quad \Delta P_a = [\text{Pa}] \quad F_a = [\text{mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}] \quad \overline{F}_a = [\text{mol m}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}]$$
Membrane properties

Separation and permeation are two opposing requirements therefore an optimal compromise has to be reached.
Membrane properties

Separation and permeation are two opposing requirements therefore an optimal compromise has to be reached.

The resistance of a membrane can be reduced by decreasing its thickness. However, it is really difficult to coat extremely thin membrane without defects. Microporous silica membranes prepared via sol-gel can be as thin as 30 nm.
Exercise 2a.

Water-gas-shift is a slightly exothermic equilibrium reaction that allows to convert carbon monoxide to carbon dioxide with hydrogen production.

\[ \text{H}_2\text{O} + \text{CO} \rightleftharpoons \text{CO}_2 + \text{H}_2 \]

- How do you think a membrane can be useful in this reaction?

Royal Dutch-Shell in the past years had tried to develop a process to convert conventional fuel to hydrogen in a vehicle. Water-gas-shift is the final step of this process. Two research groups had to develop a silica membrane for this application.
Exercise 2b.

- Research group 1 developed a silica membrane and tested it at 500 °C: first with pure hydrogen ($\Delta P = 2$ bar) and then with pure CO$_2$ ($\Delta P = 2$ bar), obtaining the following results: $F_{H2} = 4 \times 10^{-7}$ mol s$^{-1}$ m$^{-2}$ Pa$^{-1}$ and $F_{CO2} = 8 \times 10^{-9}$ mol s$^{-1}$ m$^{-2}$ Pa$^{-1}$. What is the theoretical separation factor $H_2/CO_2$ for this membrane?

$$F_{H2}/F_{CO2} = 50$$

- Research group 2 fabricated a different membrane and tested it in the same experimental conditions used by group 1. The second membrane showed $F_{H2} = 2.4 \times 10^{-6}$ mol s$^{-1}$ m$^{-2}$ Pa$^{-1}$ and $F_{CO2} = 1.2 \times 10^{-7}$ mol s$^{-1}$ m$^{-2}$ Pa$^{-1}$. What is the theoretical $H_2/CO_2$ selectivity for this membrane?

$$F_{H2}/F_{CO2} = 20$$

- Which of the two membranes do you think is the best for this application?

$$F_{a/b} = \frac{F_a}{F_b}$$

2 minutes
- High hydrogen production rates
- Reduced space

Conventional fuel to hydrogen in a vehicle.

Ideal membranes

Dense membranes

High selectivity
- Reduced pollution in urban areas

H₂ Permeance

H₂/CO₂ Selectivity

BARDONECCHIA 2016, MOLECULES @ SURFACES
• Research group 1 developed a silica membrane and tested it at 500 °C first with pure hydrogen (ΔP = 2 bar) and then with pure CO2 (ΔP = 2 bar), obtaining the following results: $F_{H2} = 4 \times 10^{-7}$ mol s$^{-1}$ m$^{-2}$ Pa$^{-1}$ and $F_{CO2} = 8 \times 10^{-9}$ mol s$^{-1}$ m$^{-2}$ Pa$^{-1}$. What is the theoretical separation factor $H2/CO2$ for this membrane? $\frac{F_{H2}}{F_{CO2}} = 50$

Exercise 2c.

• The membrane material developed by Group 1 was coated in the inner part of a tube with area of 0.018 m$^2$ and tested with a H$_2$/CO$_2$ mixture at 500 °C. The average H$_2$/CO$_2$ molar ratio inside the membrane was 1:1 mol/mol. The absolute pressure of the feed side was 3 bar while at the permeate was ~1 bar. At the permeate side the molar flow rate measured to be $1.4 \times 10^{-3}$ and $7 \times 10^{-5}$ mol s$^{-1}$ for of H$_2$ and CO$_2$, respectively. What is the separation factor of this membrane?

$$\alpha = \frac{P_{CO2,retentate}}{P_{H2,retentate}} \times \frac{P_{H2,permeate}}{P_{CO2,permeate}} = 1 \times \frac{1.4 \times 10^{-3}}{7 \times 10^{-5}} = 20$$

• Why these results are so different from those obtained in the first test?
Gas transport

Many mechanisms have been proposed based on various interaction and diffusion processes.

These mechanisms are in broad terms distinguished by the ratio of the mean free path length $\lambda$ and the diameter $d_p$.

As the pore diameter becomes smaller the interactions of gas molecules at pore surface become larger. Therefore, the state of the permeating gas molecule changes from a “gaseous state” to a “trapped state”.

Gas transport in membranes can occur through a number of possible mechanisms:

- **Bulk flow**
- **Knudsen diffusion**
- **Surface diffusion**
- **Gas-translational diffusion**
- **Solid state diffusion**
Extrusion

- Cylindrical symmetry: tubes, rods, capillaries
- Products with controlled cross-section (high tolerance)

MACROporous support
a) Viscous flow

Gas transport in porous materials occurs according to different mechanisms, depending on the size and shape of the pores.

In macropores the mean free path of a molecule is far smaller than the pore diameter. Thus a gas molecule has a higher chance to collide with another gas molecule than with the pore wall.

The Hagen-Poiseuille law is a general rule that is verified for macroscopic phenomena, such as the flux of a liquid in a pipe. In the viscous regime no gas separation is possible.

\[ J_{\text{viscous}} = \frac{\varepsilon d_p^2 \bar{P} \Delta P}{\tau 32\eta RT L} = \frac{n\pi d_p^4 \bar{P} \Delta P}{\tau 128\eta RT L} \]

\[ \varepsilon = \frac{n\pi d_p^2}{4} = \text{pore density} \]

\[ \tau = \text{pore tortuosity} \]
b) Knudsen diffusion

In mesopores the mean free path of a gas molecule is larger than the size of the pore. The interaction gas molecule-pore wall is therefore more important than the interaction molecule-molecule.

In this case the transport occurs following the Knudsen law:

\[ J_{\text{Knudsen},a} = \frac{2}{3} \frac{\bar{v}_a}{\tau RT} \frac{\Delta p_a}{L} \]

where \( \bar{v}_a \) is the mean molecular velocity of a species “a” in a pore of radius \( r \).

According to the kinetic theory of ideal gases:

\[ \bar{v}_a = \sqrt{\frac{8RT}{\pi M_a}} \]

Therefore, assuming that the pressure gradient is constant across the membrane, the gas flux of species “a” in a mesoporous membrane is:

\[ J_{\text{Knudsen}} = K \left( \frac{1}{M_a RT} \right) \frac{\Delta P_a}{L} \quad F_{\text{Knudsen}} = K' \left( \frac{1}{M_a RT} \right) \quad F_{a/b} = \sqrt{\frac{M_b}{M_a}} \]
Gas transport

**MESOporous interlayer**

\( \gamma \)-alumina is a mesoporous material commonly used in the preparation of ceramic membranes.

Permeance of 6 probe molecules through a \( \gamma \)-alumina disk.

BARDONECCHIA 2016, MOLECULES @ SURFACES
Exercise 3.

The uranium enriched in U$^{235}$ is required to produce a controlled nuclear reaction.

Several different processes may be used to enrich uranium:
• Membrane permeation
• Centrifuge
• Laser Separation

In the past the enrichment of uranium was attained by Knudsen flow through porous $\gamma$-alumina membranes. In this process $^{235}\text{UF}_6$ was separated from $^{238}\text{UF}_6$.

Question: what is the ideal separation factor for the uranium enrichment process (F = 18.998 amu; U$^{235} = 235.043$ amu; U$^{238} = 238.051$ amu).

$$F_{235/238} = \sqrt{\frac{238.051 + 6 \times 18.998}{235.043 + 6 \times 18.998}} = \sqrt{\frac{352.039}{349.031}} = 1.0043$$
MESOporous interlayer

Boehmite sol

Viscosity $[\text{mPa}\cdot\text{s}]$

Shear rate $[\text{s}^{-1}]$

S1+S2

PVA solution (S2)

boehmite sol (S1)
MESOporous interlayer
C) Surface diffusion

The transport in a microporous medium can be described as a **surface diffusion mechanism**; consequently the general Fick law can be applied:

\[ J = -D \frac{dC}{dz} \]

For microporous membranes this equation can be written as:

\[ J_a = K_0 D_0 \exp \left\{ -\frac{E_m - Q_{st}}{RT} \right\} \frac{\Delta P}{L} \]

\[ F_a = F_{0,a} \exp \left\{ -\frac{E_a}{RT} \right\} \]

\( E_a \) is the apparent activation energy. The \( E_a \) value is empirically estimated for each species measuring the temperature dependence of permeance. \( E_a \) can be positive or negative and it is considered as sum of two contributions: the **heat of absorption** \( (Q_{st}) \) and the positive **mobility energy** \( (E_m) \).

\[ E_a = E_m - Q_{st} \]
Hydrogen separation

**Ea [KJ·mol⁻¹]**

<table>
<thead>
<tr>
<th>Material</th>
<th>He</th>
<th>H₂</th>
<th>CO₂</th>
<th>Calcination T [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb₂O₅-doped SiO₂</td>
<td>19.1±0.3</td>
<td>15.3±0.7</td>
<td>-14.2±0.8</td>
<td>500</td>
</tr>
<tr>
<td>SiO₂</td>
<td>7 -23</td>
<td>7.6-8</td>
<td>-4 ; -2</td>
<td>400 ; 600</td>
</tr>
<tr>
<td>ZrO₂-doped SiO₂</td>
<td>22</td>
<td>44</td>
<td></td>
<td>550</td>
</tr>
</tbody>
</table>

**BARDONECCHIA 2016, MOLECULES @ SURFACES**
Fabrication

Introduction

Calcination (400 - 600 °C)

Coating

HNO₃ → TEOS → H₂O

r.t. - 60 °C

2 - 24 h
### MICROporous active layer

<table>
<thead>
<tr>
<th></th>
<th>REACTION-LIMITED</th>
<th>BALLISTIC</th>
<th>DIFFUSION-LIMITED</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>MONOMER-CLUSTER</strong></td>
<td>EDEN</td>
<td>VOLD</td>
<td>WITTEN-SANDER</td>
</tr>
<tr>
<td>D = 3.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>CLUSTER-CLUSTER</strong></td>
<td>RLCA</td>
<td>SUTHERLAND</td>
<td>DLCA</td>
</tr>
<tr>
<td>D = 2.09</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Diffusing gas molecules have enough kinetic energy to escape the surface potential....

.... but cannot readily do so because of the presence of a pore wall on the other side.
This is a mechanism in which there is a combination of the Knudsen diffusion model and the surface diffusion model.

Both surface diffusion and gas-translation have contributions

The formula of the permeance in this regime is obtained from the Knudsen diffusion model by introducing the probability for diffusion through the micropore (\( \rho \))

\[
F = \frac{\varepsilon d_p \rho_g}{\tau L} \left( \frac{8}{\pi MRT} \right)^{1/2} \exp \left( -\frac{\Delta E}{RT} \right)
\]
d) Translational diffusion

Zeolite membranes


J. Membrane Sci. 2011, 371, 197–210
e) Solution-diffusion

Examples:

- Perovskite membranes for oxygen separation
- Metallic membranes for hydrogen separation
- Hydrogen and helium permeation in dense silica glasses

For solid-state permeation the molecules permeating through the solid are considered to reside in solubility sites and to be in equilibrium with the gaseous state.

Permeance = solubility × diffusivity
Contribution of the support

\[ R_{TOT} = R_1 + R_2 \]

\[ R = \frac{1}{F} \quad \text{(Pa m}^2\text{s mol}^{-1}) \]

\[ \frac{1}{F_{tot}} = \frac{1}{F_{support}} + \frac{1}{F_{silica}} \]
Different mechanisms in the support layer
Exercise 2c.

- Research group 1 developed a silica membrane and tested it at 500 °C first with pure hydrogen (ΔP = 2 bar) and then with pure CO₂ (ΔP = 2 bar), obtaining the following results: $F_{H_2} = 4 \times 10^{-7}$ mol s⁻¹ m⁻² Pa⁻¹ and $F_{CO_2} = 8 \times 10^{-9}$ mol s⁻¹ m⁻² Pa⁻¹. What is the theoretical separation factor $H_2/CO_2$ for this membrane? $\frac{F_{H_2}}{F_{CO_2}} = 50$

- The membrane material developed by Group 1 was coated in the inner part of a tube with area of 0.018 m² and tested with a H₂/CO₂ mixture at 500 °C. The average H₂/CO₂ molar ratio inside the membrane was 1:1 mol/mol. The absolute pressure of the feed side was 3 bar while at the permeate was ~ 1 bar. At the permeate side the molar flow rate measured to be $1.4 \times 10^{-3}$ and $7 \times 10^{-5}$ mol s⁻¹ for H₂ and CO₂, respectively. What is the separation factor of this membrane?

$$\alpha = \frac{P_{CO_2, retentate}}{P_{H_2, retentate}} \times \frac{P_{H_2, permeate}}{P_{CO_2, permeate}} = 1 \times \frac{1.4 \times 10^{-3}}{7 \times 10^{-5}} = 20$$

- Why these results are so different from those obtained in the first test?
Gas mixtures

Onsager equations for a binary mixture:

\[
\begin{align*}
    j_{l_1} &= -L_{l_1,l_1} \nabla \tilde{\mu}_{l_1} - L_{l_1,l_2} \nabla \tilde{\mu}_{l_2} \\
    j_{l_2} &= -L_{l_1,l_2} \nabla \tilde{\mu}_{l_1} - L_{l_2,l_2} \nabla \tilde{\mu}_{l_2}
\end{align*}
\]

\[
\nabla \tilde{\mu} = \frac{d \tilde{\mu}}{dx}
\]

In Knudsen separation, the cross-coefficient, \(L_{l_1,l_2}\) is zero (the assumption is that the molecules only meet the pore walls and not each other):

\[
\begin{align*}
    j_{l_1} &= -L_{l_1} \nabla \tilde{\mu}_{l_1} \quad \text{and} \quad j_{l_2} = -L_{l_2} \nabla \tilde{\mu}_{l_2}
\end{align*}
\]

For microporous molecular transport, \(L_{l_1,l_2}\) is in general not negligible, but it is often assumed to be zero at first approximation.
An overview on the evolution of gas-selective silica membranes

Defect-free membranes

Stable membranes

Functional membranes

1980

1990

2000

2010


V. Boffa et al. 2008 ChemSusChem 1,437.


BARDONECCHIA 2016, MOLECULES @ SURFACES
Aalborg University

Department of Chemistry and Bioscience