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Transport phenomena in gas-selective silica membranes

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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:

Reverse Osmosis is an example of membrane process
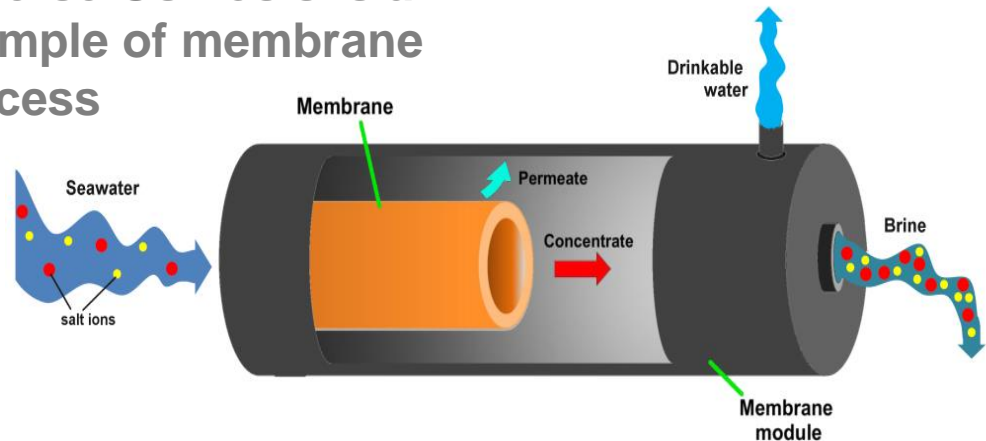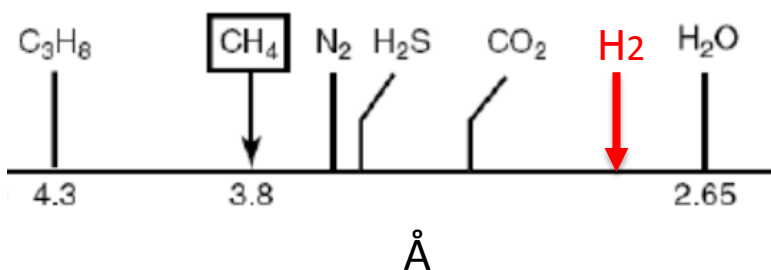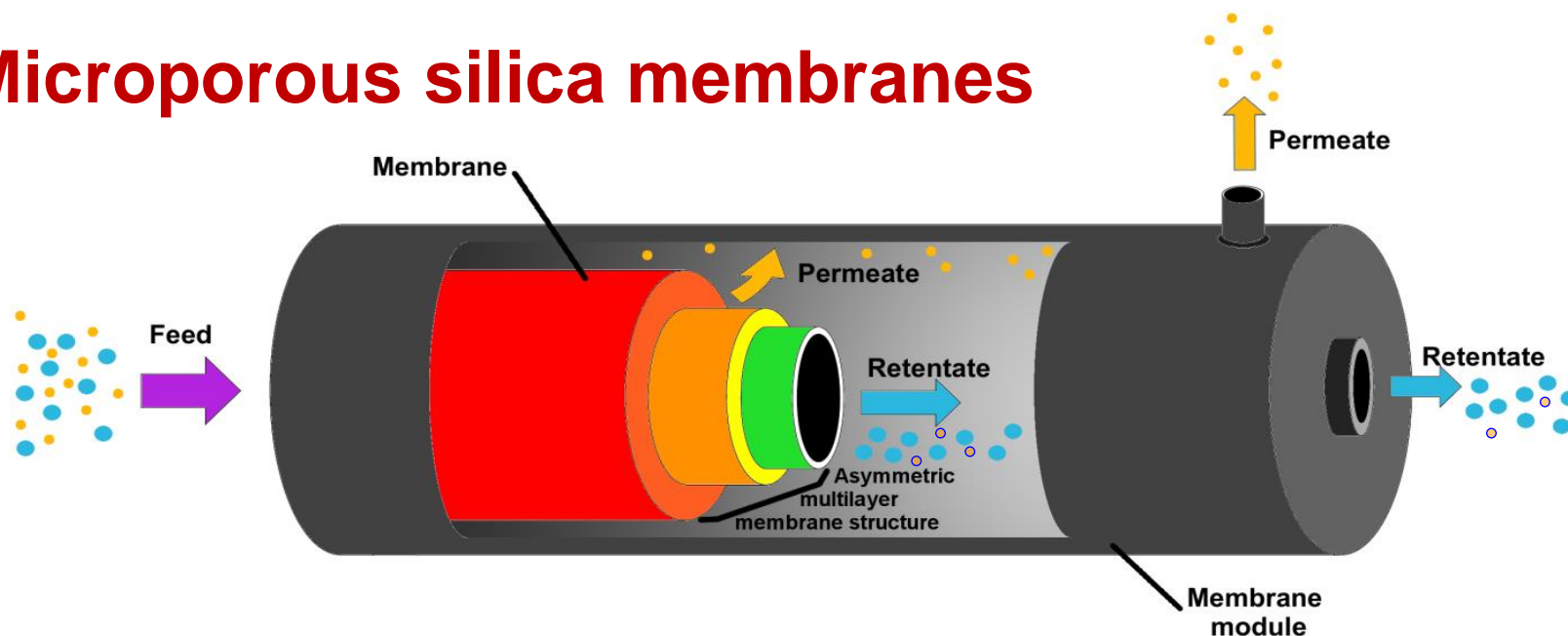

Membranes are fabricated for separating molecules, ions or colloids. Membrane processes are characterized by the fact that the feed flow is divided in two streams called **permeate** (what passes through the membrane) and **retentate** (what doesn't pass through the membrane) .

*W.J. Koros, Y.H. Ma, T. Shimidzu, Pure Appl. Chem., 68 (1996) 1479.

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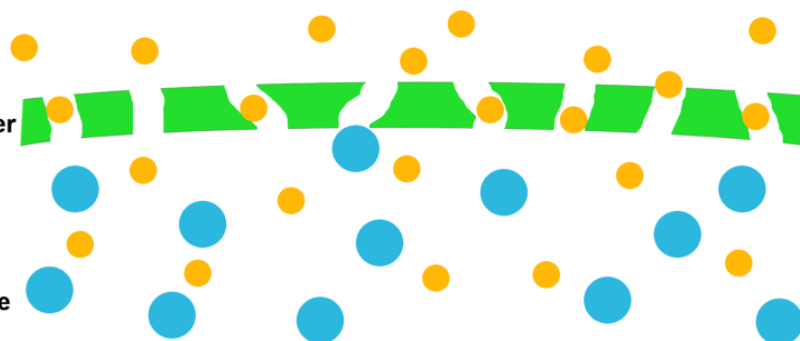
Upcoming technology platforms for green fuel production require the development of advanced molecular separation processes for recovering liquid biofuels, biomethane and hydrogen.

Gas separation	Pervaporation
• H_2 purification • CO_2 sequestration • Biogas upgrading	• Alcohol dehydration • Separation of organic solvents

CH_3CH_2OH

CO2

Dissolved CO$_2$

H2

F-Cell
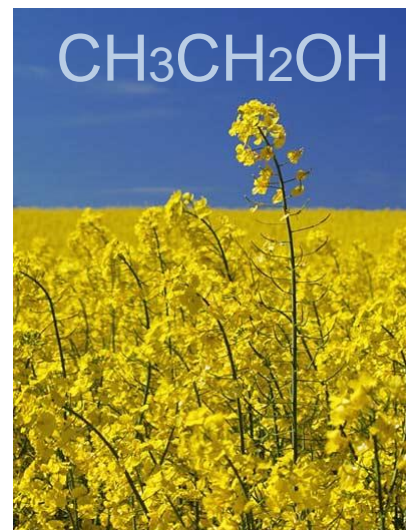
Membrane structure
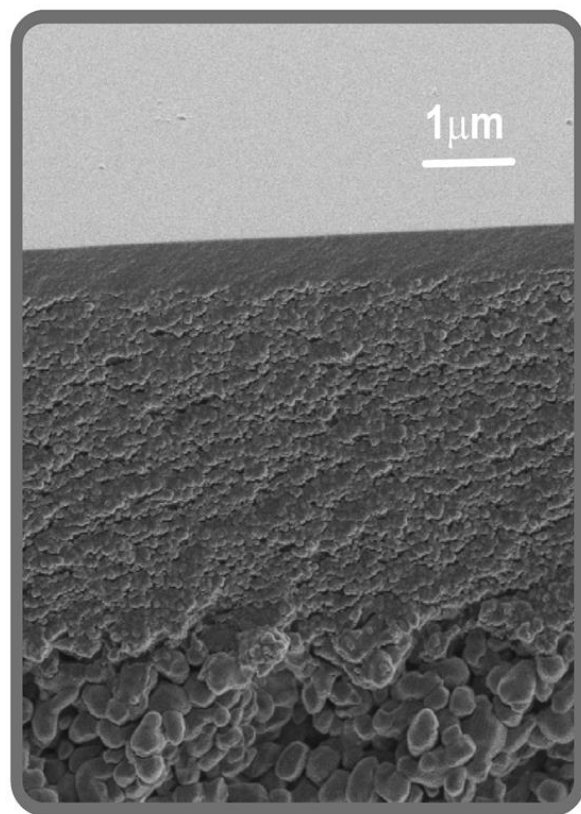
Silica top layer

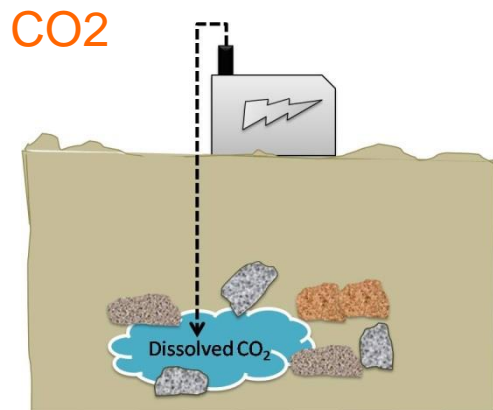γ-Alumina

α-Alumina
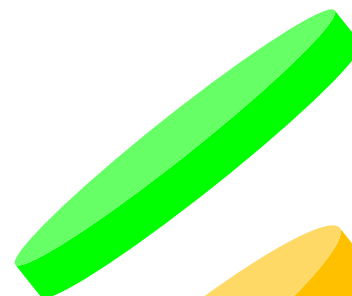
Microporous
Pore diameter = 2 nm

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

ΔP_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** (α):

$$\alpha = \frac{x_{retentate}}{y_{retentate}} \cdot \frac{y_{permeate}}{x_{permeate}}$$

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 $\Delta P = 4$ bar ($4 \cdot 10^5$ Pa) is 0.4 mol s^{-1} m^{-2} . Calculate the membrane permeance.

$$F_a = \frac{J_a}{\Delta P_a}$$

F_{H2} = 0.4 (mol s^{-1} m^{-2}) / 4 $\cdot 10^5$ Pa =
1 $\cdot 10^{-6}$ mol m^{-2} s^{-1} Pa^{-1}

J_a = [mol m^{-2} s^{-1}] ΔP_a = [Pa] F_a = [mol m^{-2} s^{-1} Pa^{-1}]

Exercise 1b. :

- Membrane 1 has thickness of 250 nm and H_2 permeance of **1 ·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.

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

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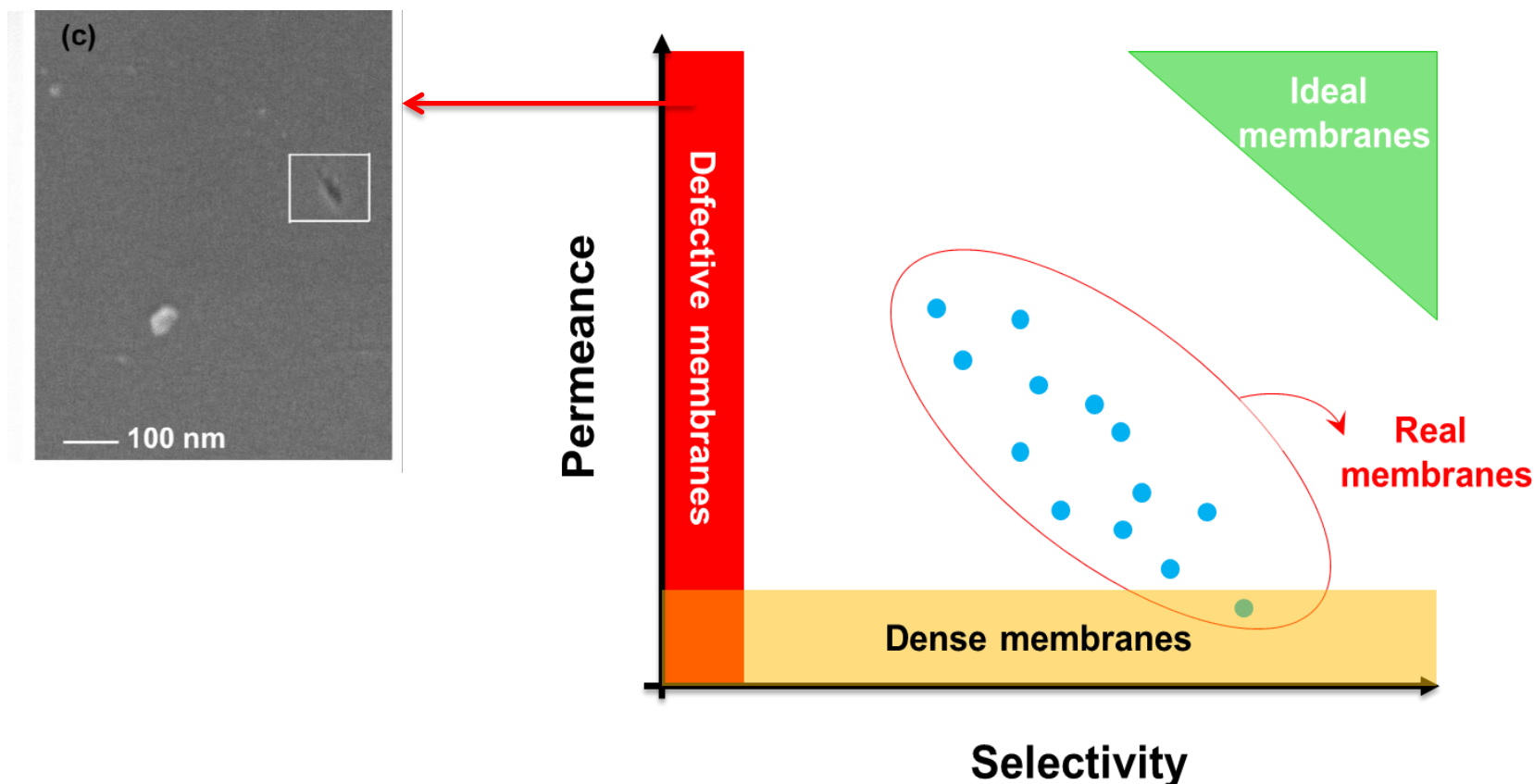
$$\overline{F_a} = F_a \cdot L$$

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

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

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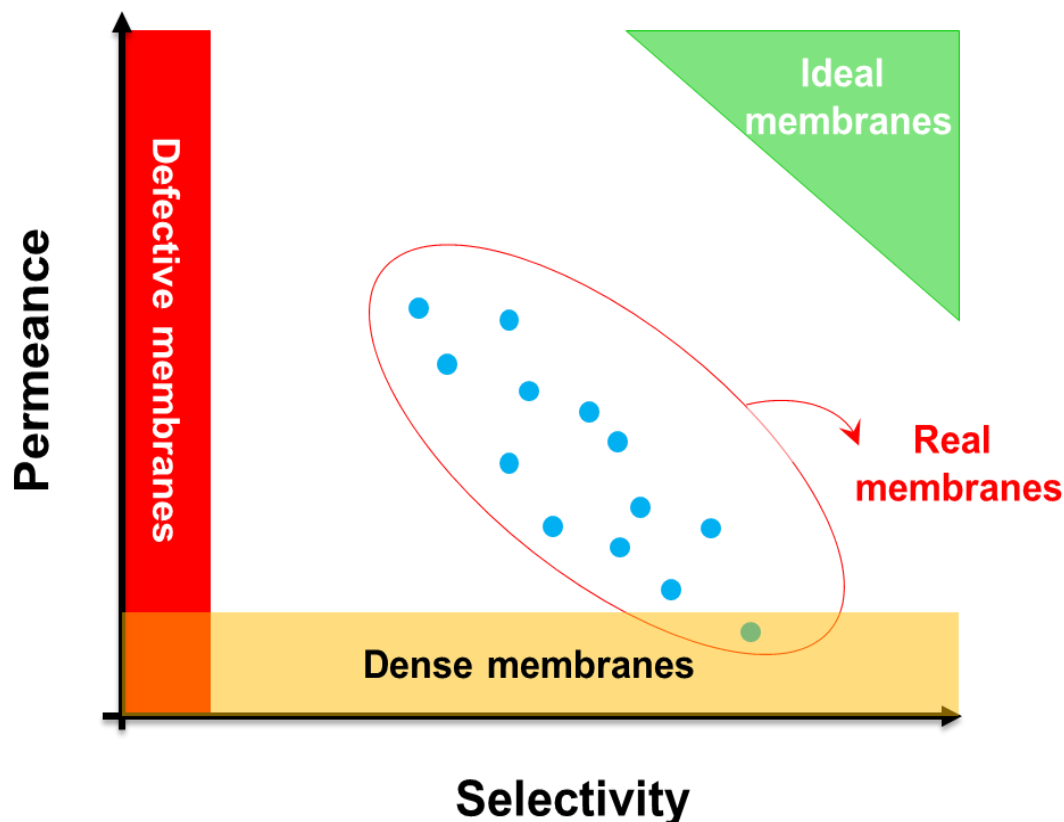
Membrane properties

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.

$$H_2O + CO \rightleftarrows CO_2 + H_2$$
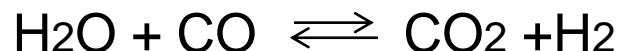
- How do you think a membrane can be useful in this reaction?

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 (ΔP = 2 bar) and then with pure CO_2 (ΔP = 2 bar), obtaining the following results: F_{H2} = 4×10⁻⁷ mol s⁻¹ m⁻² Pa⁻¹ and F_{CO2} = 8 × 10⁻⁹ mol s⁻¹ m⁻² Pa⁻¹. What is the theoretical separation factor H_2/CO_2 for this membrane?

$$\frac{F_{H2}}{F_{CO2}} = 50$$

- 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 ×10⁻⁶ mol s⁻¹ m⁻² Pa⁻¹ and F_{CO2} = 1.2×10⁻⁷ mol s⁻¹ m⁻² Pa⁻¹. What is the theoretical H_2/CO_2 selectivity for this membrane?

$$\frac{F_{H2}}{F_{CO2}} = 20$$

- Which of the two membranes do you think is the best for this application?
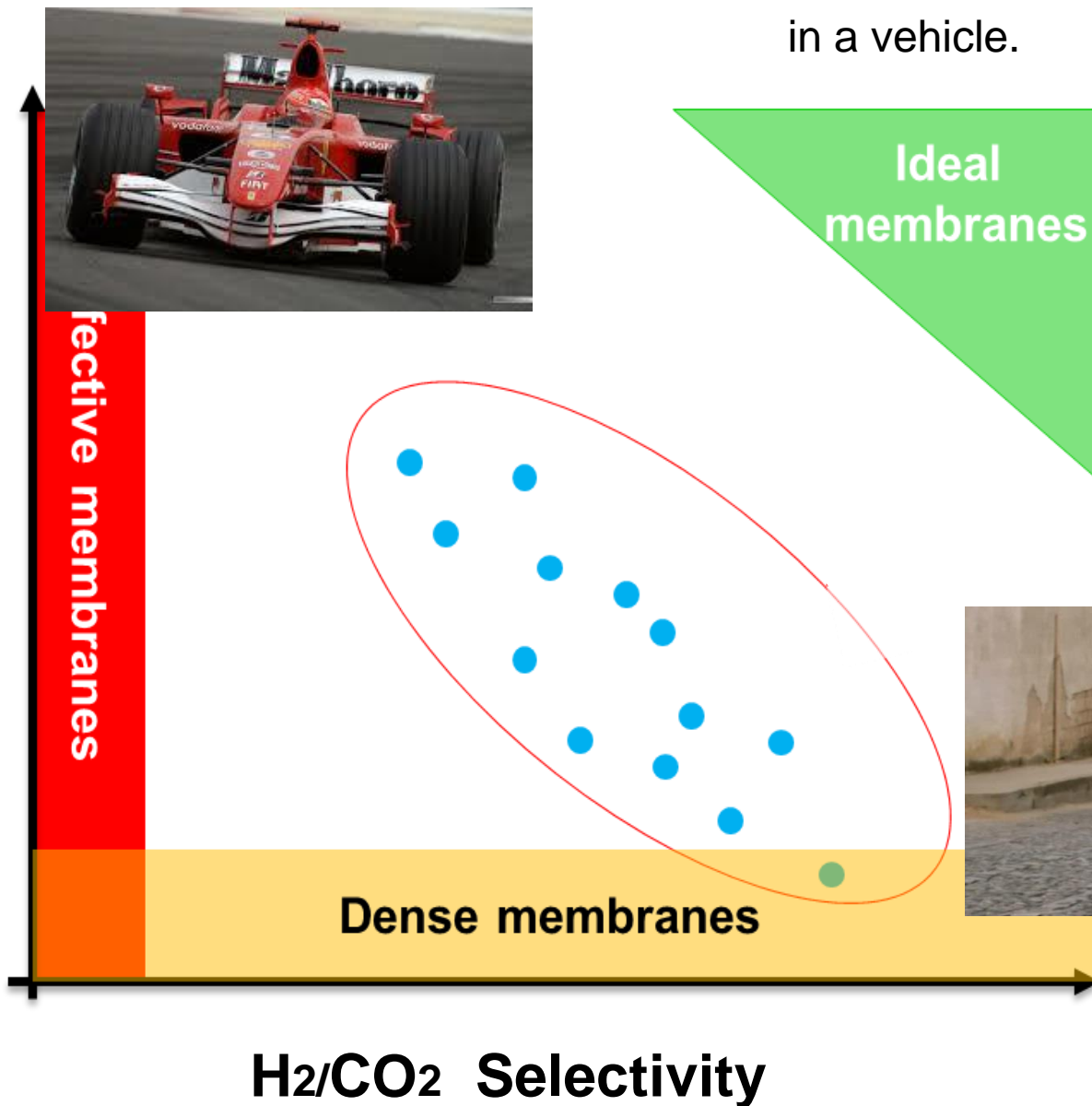
$$F_{a/b} = \frac{F_a}{F_b}$$

2 minutes

- High hydrogen production rates
- Reduced space

Conventional fuel to hydrogen in a vehicle.

Ideal membranes

fective membranes

H₂ Permeance

Dense membranes

H₂/CO₂ Selectivity

- High selectivity
- Reduced pollution in urban areas

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

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

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 1.4×10^{-3} and 7×10^{-5} mol s^{-1} for of H_2 and CO_2, respectively. What is the separation factor of this membrane?

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

- Why these results are so different from those obtained in the first test?
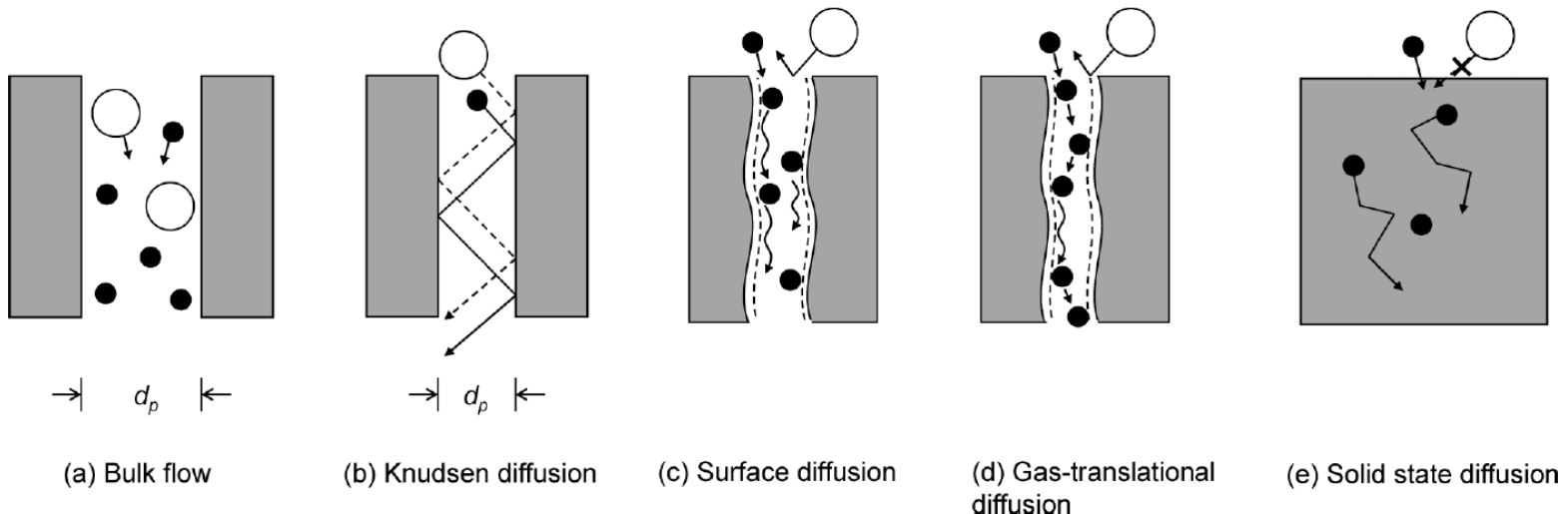
2 minutes

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 λ and the diameter d_p.

As the pore diameter becomes smaller the interactions of **gas molecules @ 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:

(a) Bulk flow   (b) Knudsen diffusion   (c) Surface diffusion   (d) Gas-translational diffusion   (e) Solid state diffusion

Extrusion

- Cylindrical symmetry: tubes, rods, capiollaries

- Products with controlled cross-section (high tolerance)

Silica top layer

γ-Alumina

α-Alumina
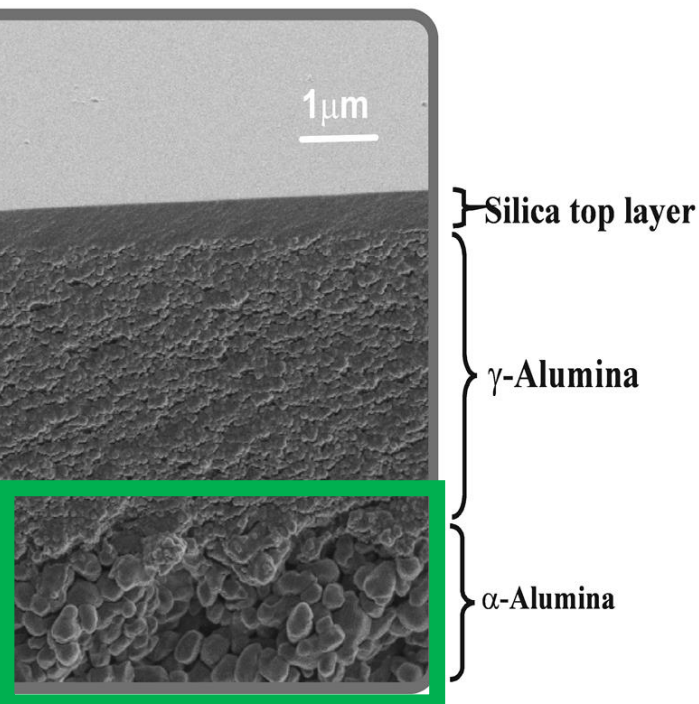
MACROporous support

Extrusion forms

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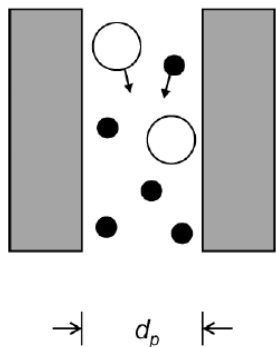
Gas transport in porous materials occurs according to different mechanisms, depending on the size and shape of the pores.

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.

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

$$\varepsilon = \frac{n\pi d_p^2}{4} = pore\ density$$

$$\tau = pore\ tortuosity$$

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.

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:

1871 Hasmark
1949 København

$$J_{Knudsen,a} = \frac{2}{3} \bar{\upsilon}_a \frac{\varepsilon r}{\tau RT} \frac{\Delta p_a}{L}$$
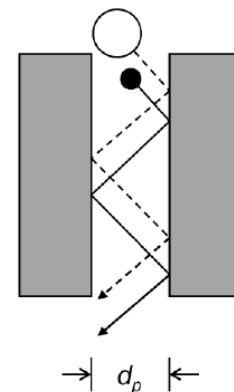
where υ_a is the mean molecular velocity of a species "a" in a pore of radius r. According to the kinetic theory of ideal gases:

$$\bar{\upsilon}_a = \sqrt{\frac{8RT}{\pi M_a}}$$

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

$$J_{Knudsen} = K \sqrt{\frac{1}{M_a RT}} \frac{\Delta P_a}{L} \qquad F_{Knudsen} = K' \sqrt{\frac{1}{M_a RT}} \qquad F_{a/b} = \sqrt{\frac{M_b}{M_a}}$$

Gas transport

MESOporous interlayer

γ-alumina is a mesoporous material commonly used in the preparation of ceramic membranes.
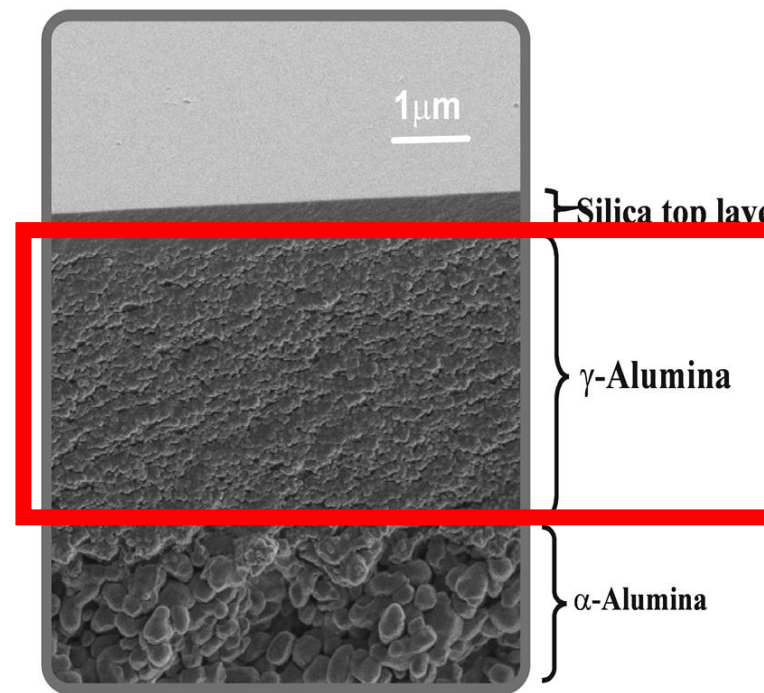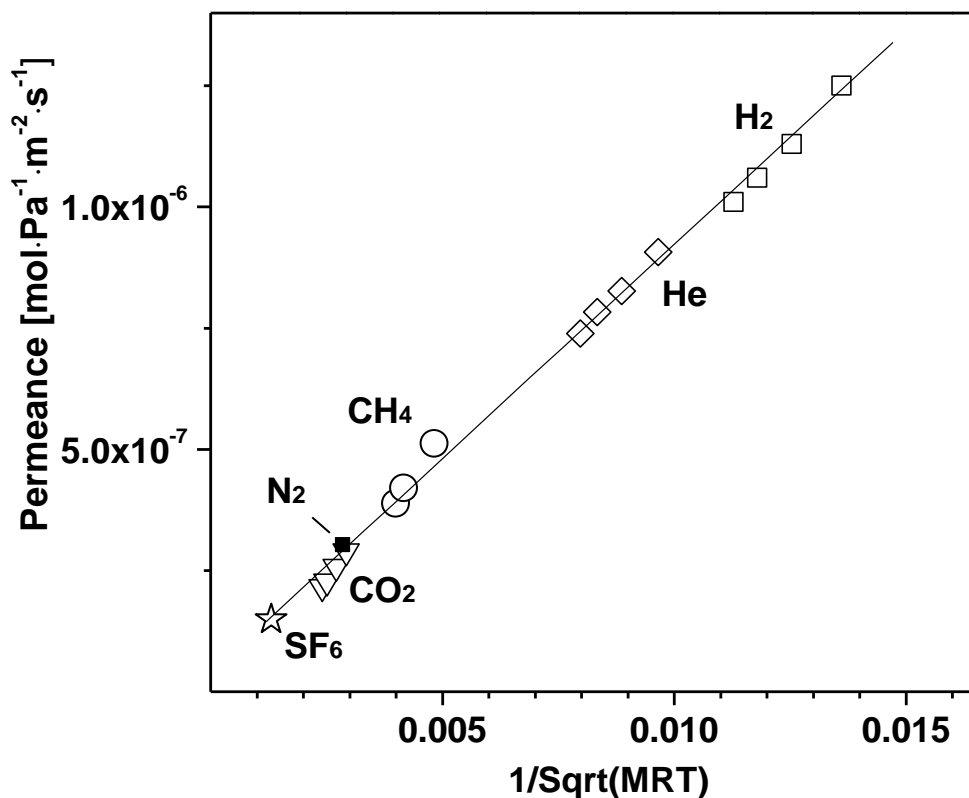
Permeance of 6 probe molecules trough a γ-alumina disk.

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
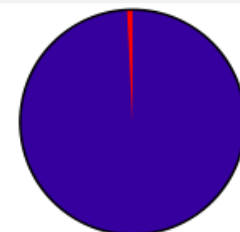
Natural uranium
> 99.2% U-238
0.72% U-235
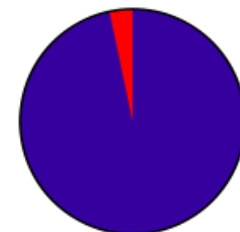
Low-enriched uranium
(reactor grade)
3-4% U-235

In the past the enrichment of uranium was attained by Knudsen flow through porous γ-alumina membranes. In this process $^{235}UF_6$ was separated from $^{238}UF_6$.

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).

2 minutes

$$F_{235/238} = \sqrt{\frac{238.051 + 6 \times 18.998}{235.0.43 + 6 \times 18.998}} = \sqrt{\frac{352.039}{349.031}} = 1.0043$$
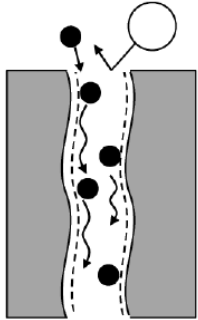
MESOporous interlayer
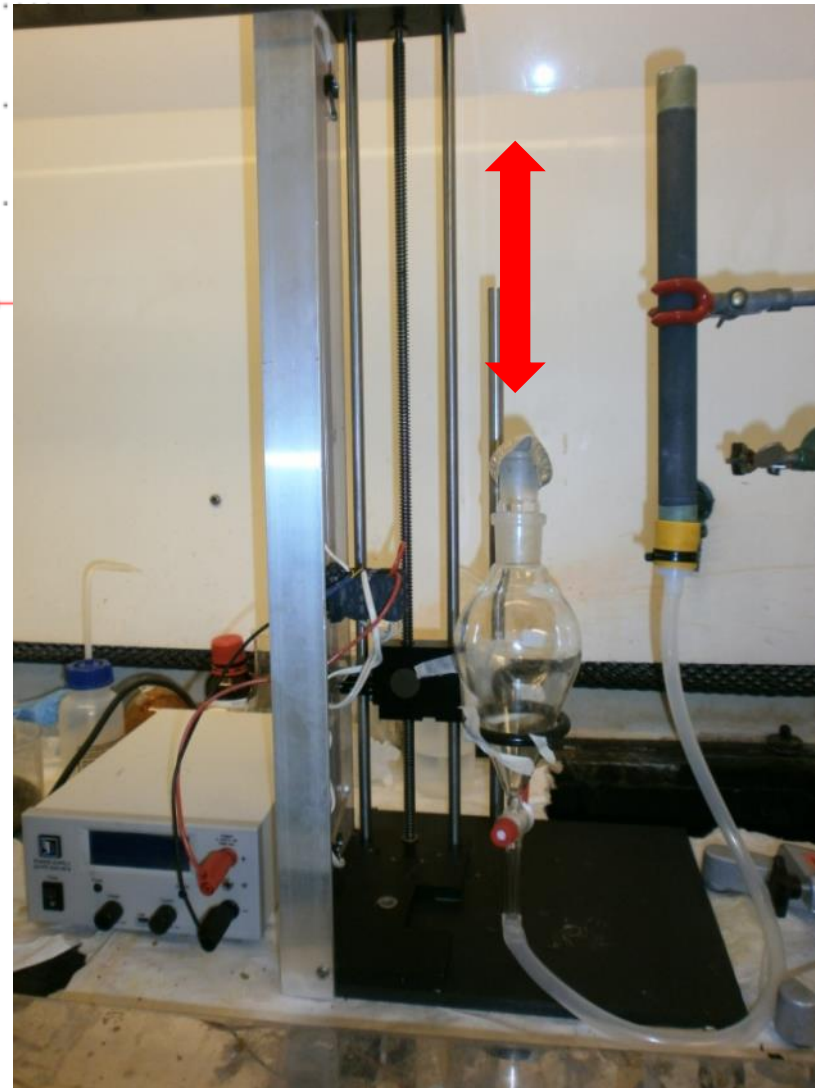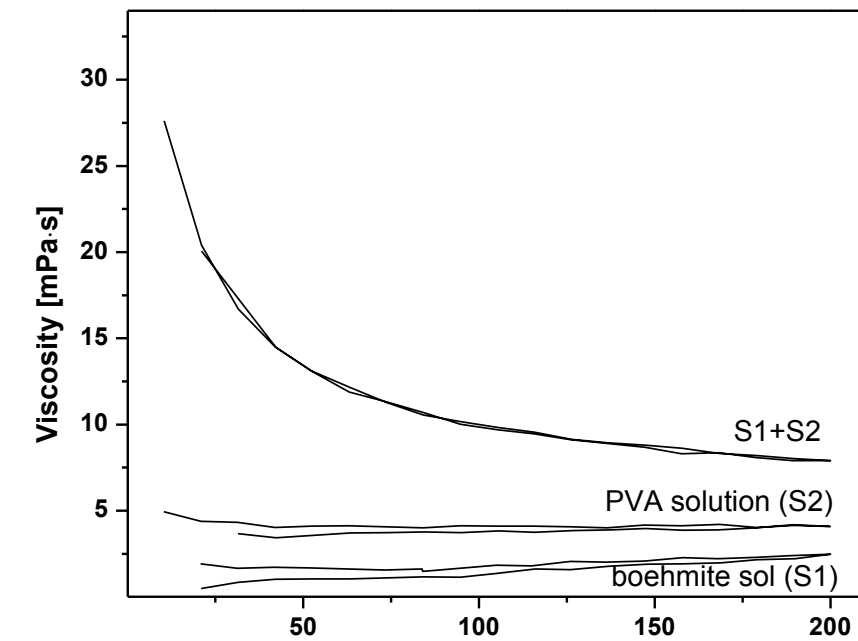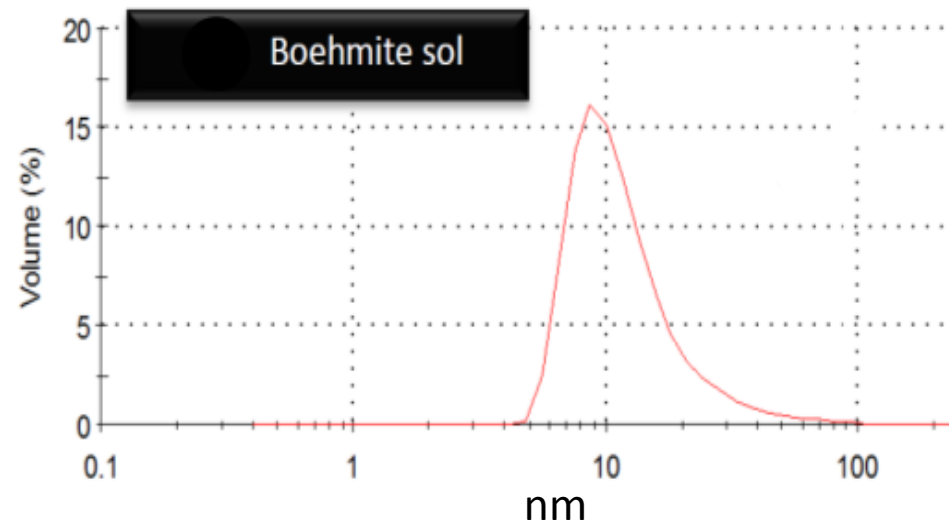
MESOporous interlayer
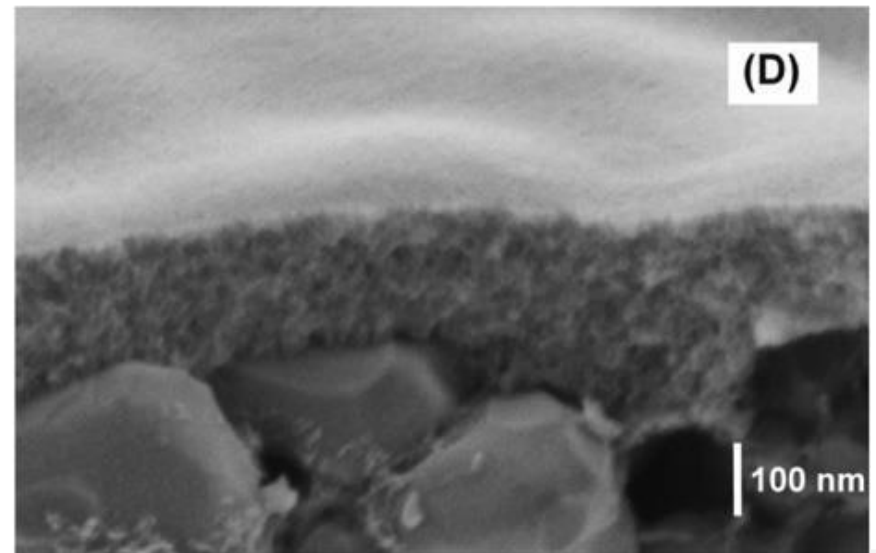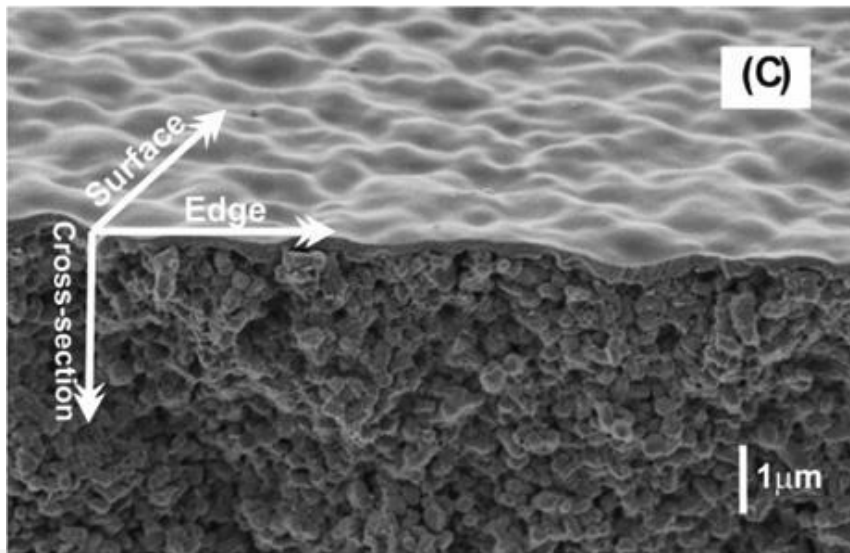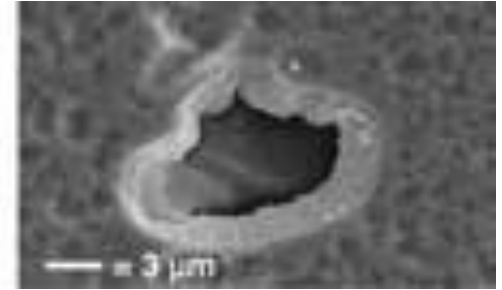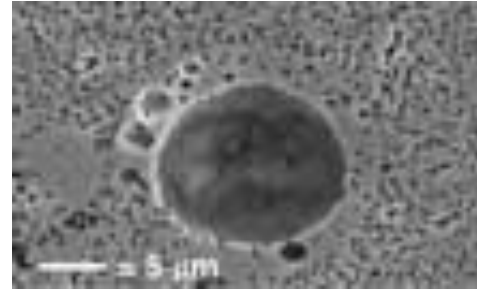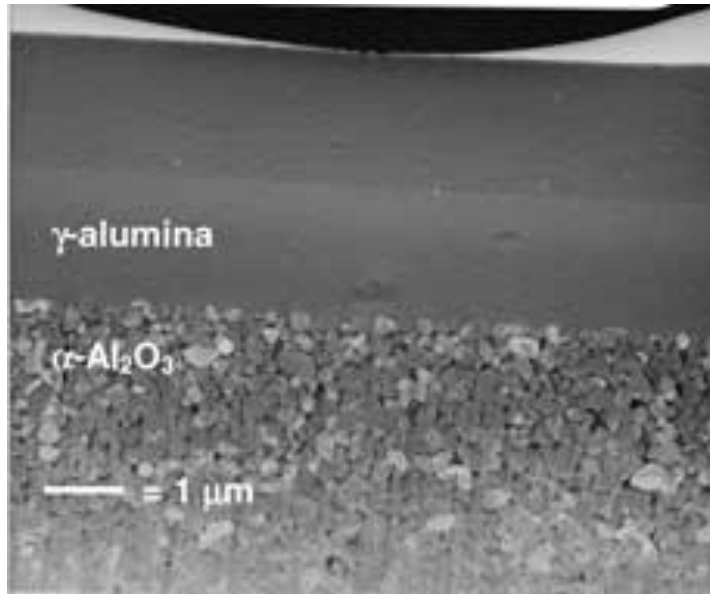
C) Surface diffusion

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:

$$J_a = K_0 D_0 \exp\left\{-\frac{E_m - Q_{st}}{RT}\right\} \frac{\Delta P}{L} \qquad F_a = F_{0,a} \exp\left\{-\frac{E_a}{RT}\right\}$$

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).
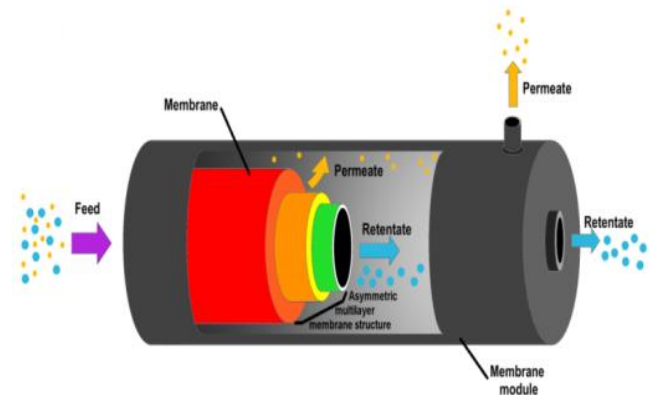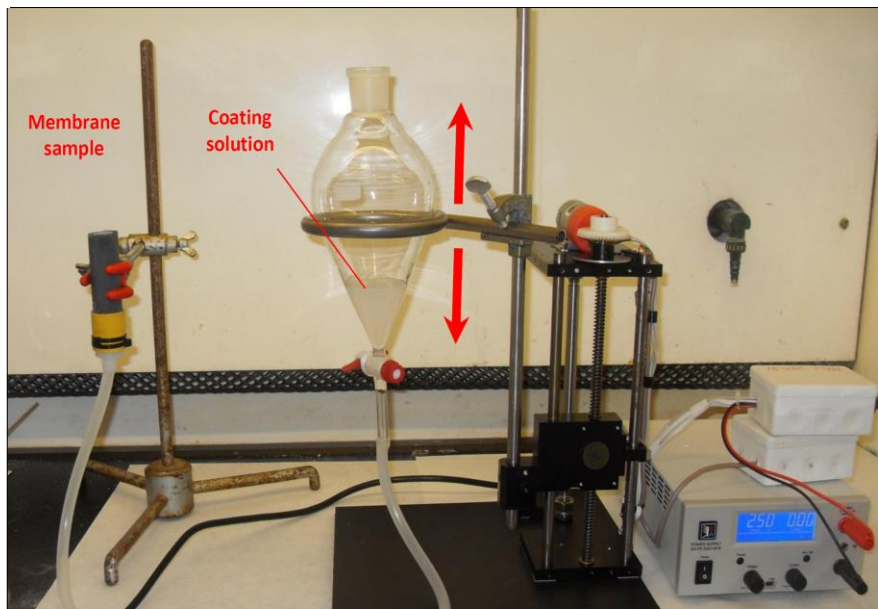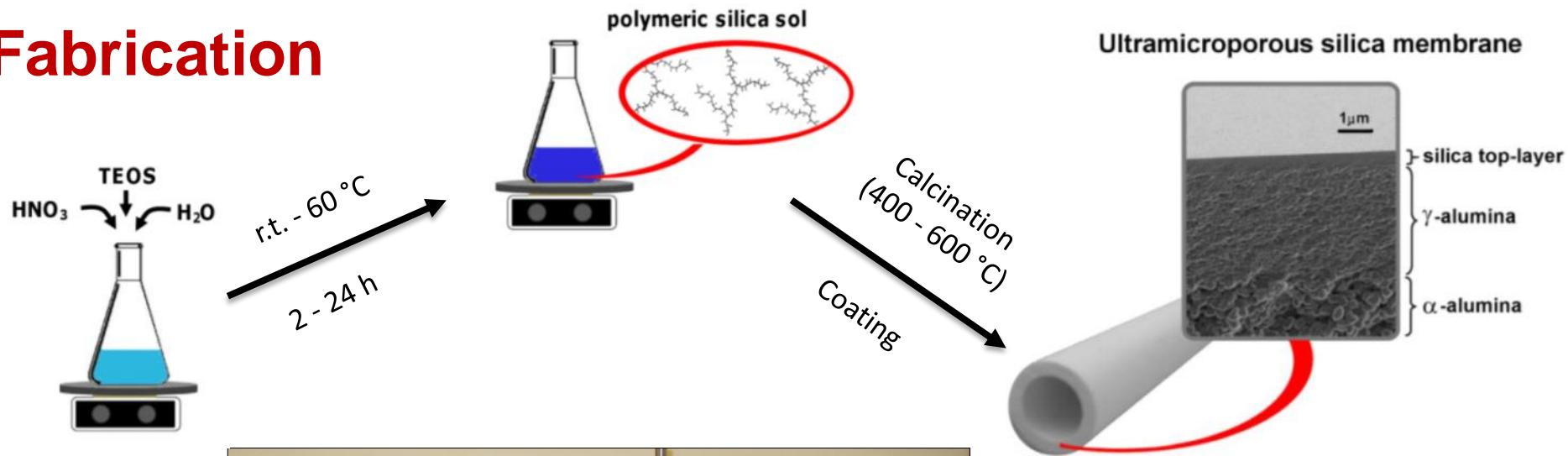
$$E_a = E_m - Q_{st}$$

Hydrogen separation
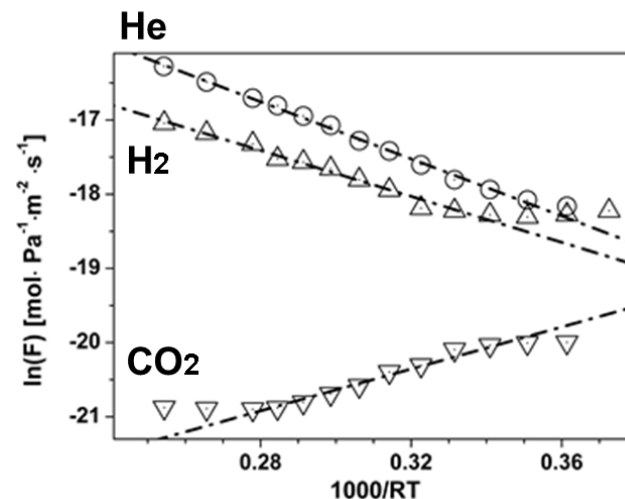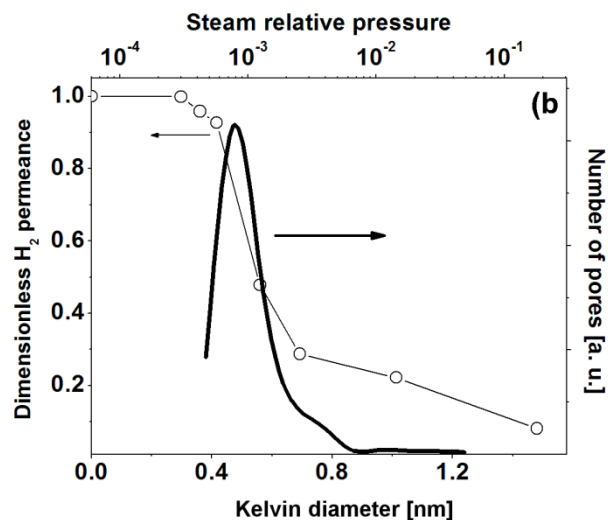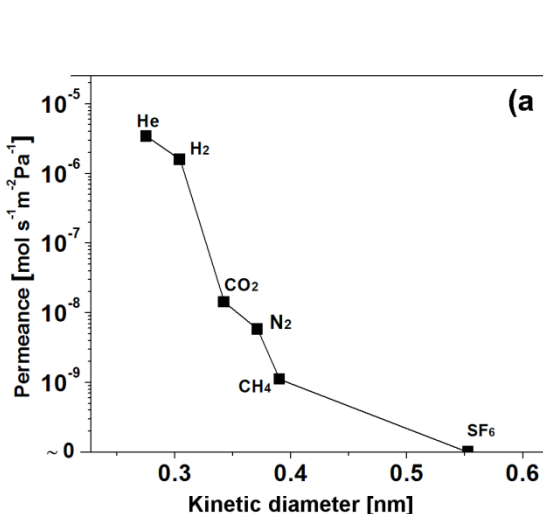
	Ea [KJ·mol^{-1}]			Calcination T [°C]
	He	H$_2$	CO$_2$	
Nb$_2$O$_5$-doped SiO$_2$	19.1±0.3	15.3±0.7	-14.2±0.8	500
SiO$_2$	7 -23	7.6-8	-4 ; -2	400 ; 600
ZrO2-doped SiO$_2$	22	44		550
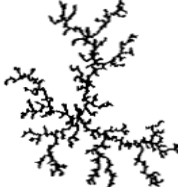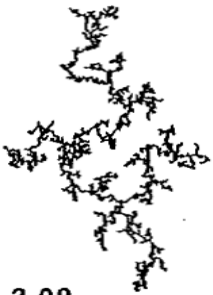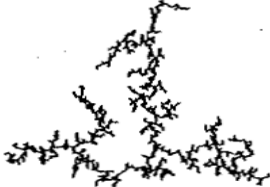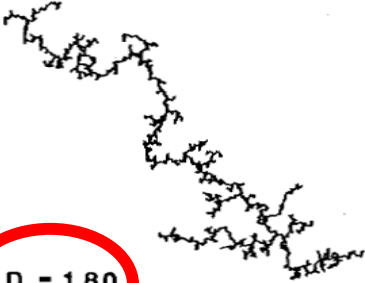
Fabrication

MICROporous active layer

	REACTION-LIMITED	BALLISTIC	DIFFUSION-LIMITED
MONOMER-CLUSTER	EDEN D = 3.00	VOLD D = 3.00	WITTEN-SANDER D = 2.50
CLUSTER-CLUSTER	RLCA D = 2.09	SUTHERLAND D = 1.95	DLCA D = 1.80
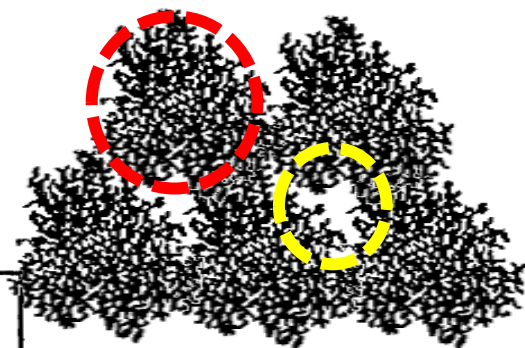
P. Meakin, *Adv. Colloid Interface Sci.* **28**, 249 (1989)
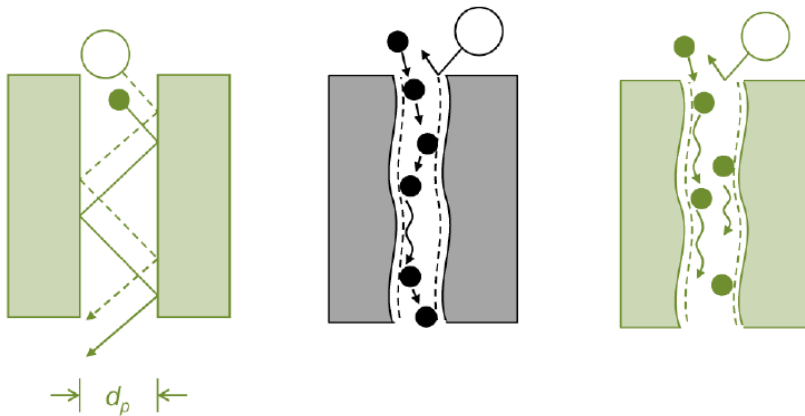
d) Translational diffusion

$$F = \frac{\varepsilon d_{\mathrm{p}} \rho_{\mathrm{g}}}{\tau L}\left(\frac{8}{\pi M R T}\right)^{1/2}\exp\left(-\frac{\Delta E}{R T}\right)$$

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.

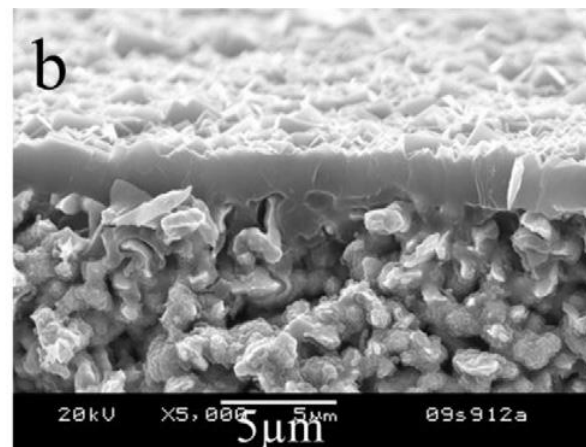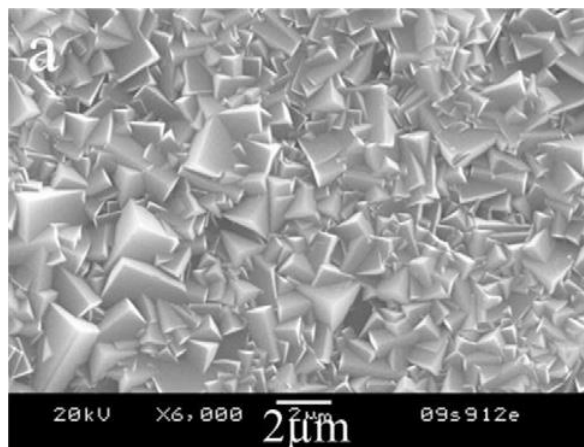Both surface diffusion and gas-translation have contributions

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

d) Translational diffusion
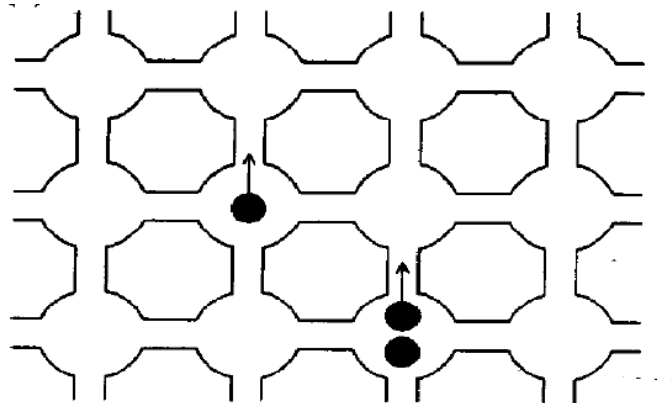
Chem. Eng. Sci. 1992, 47, 1123-1141.

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.

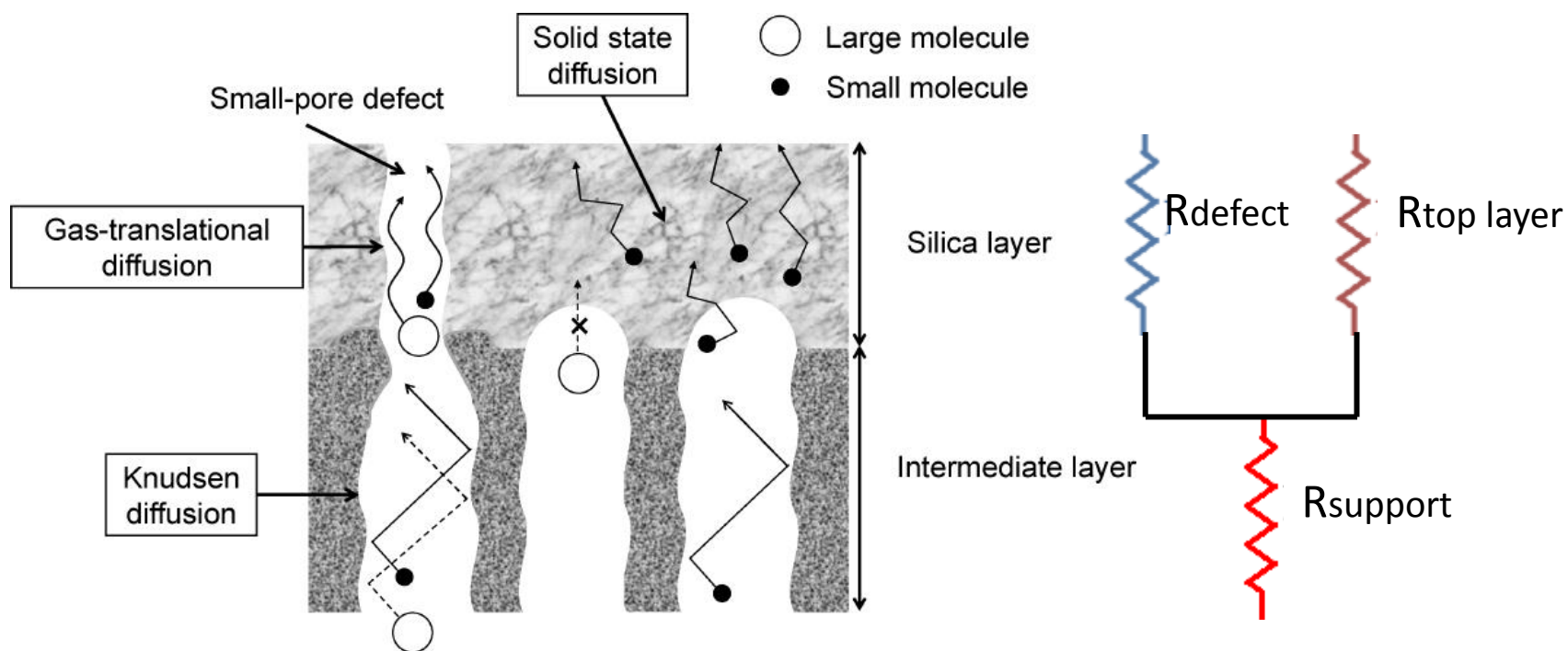Permeance = solubility × diffusivity
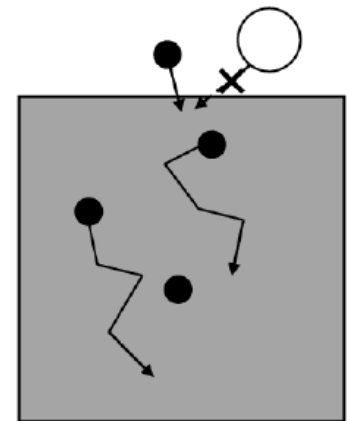
Contribution of the support
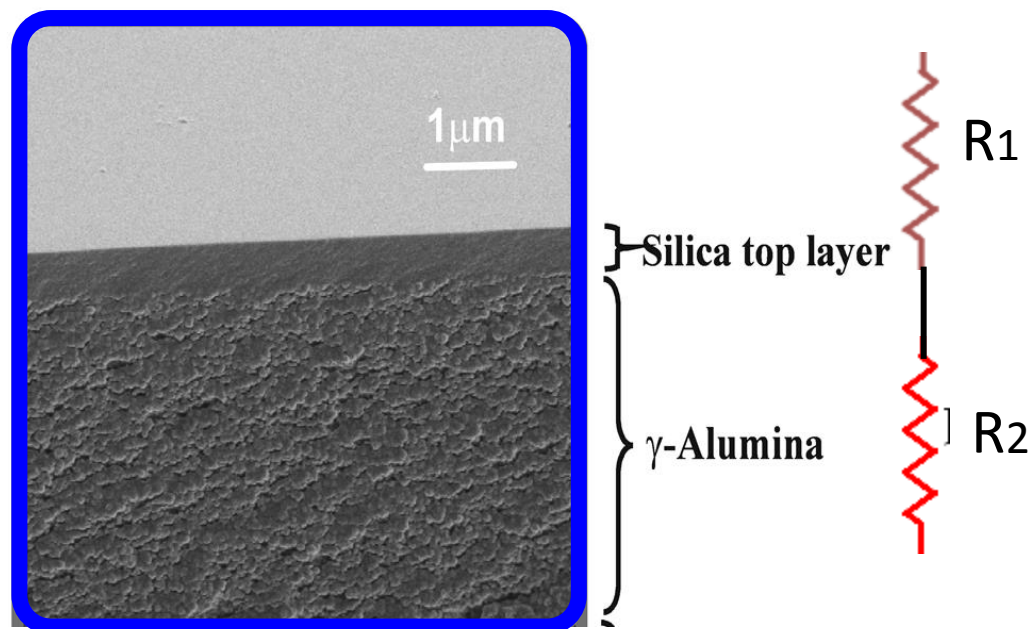
$R_{TOT} = R_1 + R_2$

$$R = \frac{1}{F} \qquad (\text{Pa m}^2 \text{ s mol}^{-1})$$

$$\frac{1}{F_{tot}} = \frac{1}{F_{support}} + \frac{1}{F_{silica}}$$

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 CO_2 (ΔP = 2 bar), obtaining the following results: F_{H2} = 4×10^{-7} mol s^{-1} m^{-2} Pa^{-1} and F_{CO2} = 8×10^{-9} mol s^{-1} m^{-2} Pa^{-1}. What is the theoretical separation factor H_2/CO_2 for this membrane?

$$\frac{F_{H2}}{F_{CO2}} = 50$$

- 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 1.4×10^{-3} and 7×10^{-5} mol s^{-1} for of H_2 and CO_2, respectively. What is the separation factor of this membrane?

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

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

2 minutes

Gas mixtures

Onsager equations for a binary mixture:

$$\begin{cases} j_{l_1} = -L_{l_1,l_1}\nabla\tilde{\mu}_{l_1} - L_{l_1,l_2}\nabla\tilde{\mu}_{l_2} \\ j_{l_2} = -L_{l_1,l_2}\nabla\tilde{\mu}_{l_1} - L_{l_2,l_2}\nabla\tilde{\mu}_{l_2} \end{cases} \qquad \nabla\tilde{\mu} = \frac{d\tilde{\mu}}{dx}$$

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):

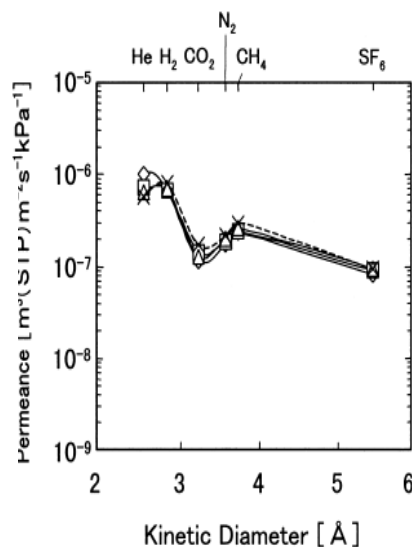$$j_{l_1} = -L_{l_1}\nabla\tilde{\mu}_{l_1} \quad \text{and} \quad j_{l_2} = -L_{l_2}\nabla\tilde{\mu}_{l_2}$$

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.

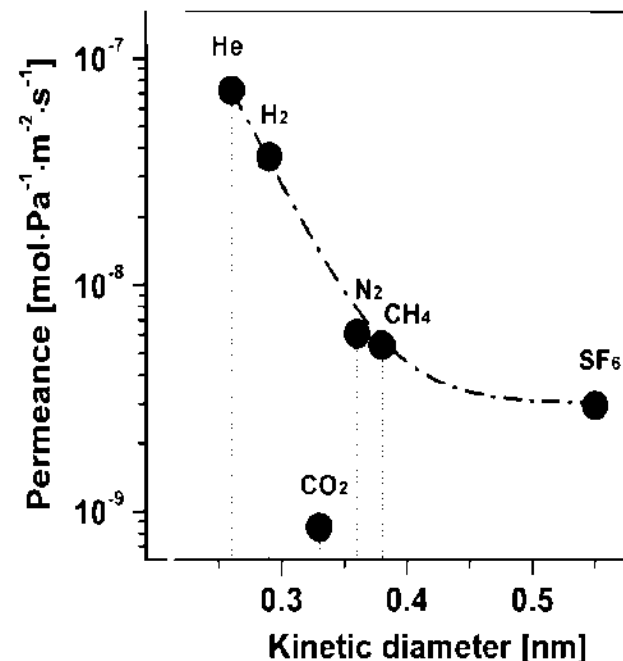# An overview on the evolution of gas-selective silica membranes
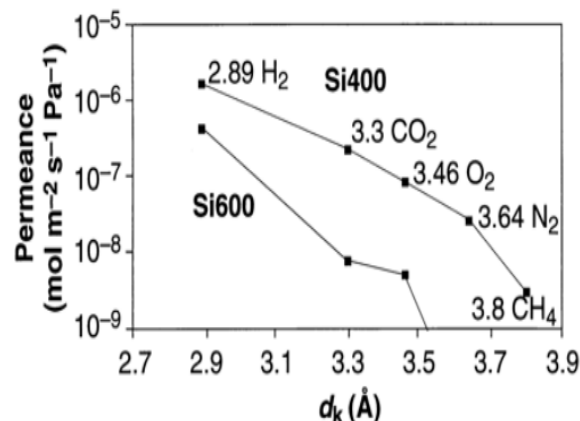
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M. Asaeda et al. **2001** J. Chem. Eng. Jap. 4, 523.

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Stable membranes

Defect-free membranes

Functional membranes

1980   1990   2000   2010

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