Concentration Polarization in hydrogen permeation through self-supported Pd-based membranes

Giuseppe BARBIERI[1], Alessio CARAVELLA[1] and Enrico DRIOLI[1,2]

[1]National Research Council - Institute on Membrane Technology, ITM-CNR,
c/o The University of Calabria, Via P. Bucci - Cubo 17C, 87036 Rende (CS), Italy.

[2]The University of Calabria - Dept. of Chemical and Materials Engineering,
Via P. Bucci - Cubo 44A, 87036 Rende (CS), Italy.

Presentation Topics

- ☐ **Motivation of the analysis**
- ☐ **Elementary step-based permeation model**
  - ✓ **Description and details**
  - ✓ **Results and comments**
- ☐ **Concentration polarization analysis**
  - ✓ **Definition of the concentration polarization coefficient CPC**
  - ✓ **Results and comments**
- ☐ **Overall conclusions**

Motivation of the analysis

The Pd-based membranes present an infinite selectivity towards hydrogen with respect to all the other chemical species.

Hence, their integration in production and purification process could lead up to significant advantages with respect to traditional equipments.

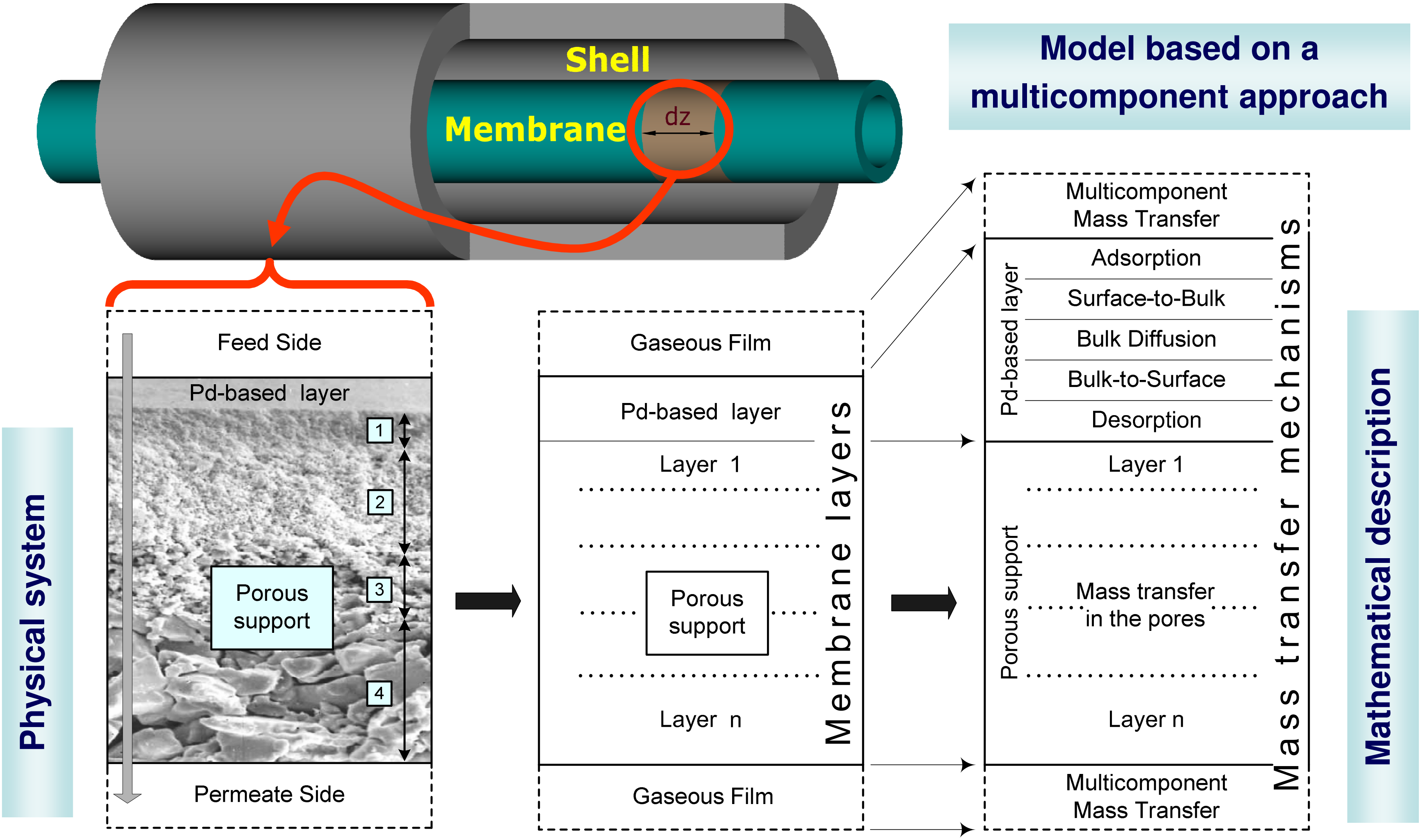
However, the possibility to use massively these membranes is related to a deep knowledge of their behaviour in different conditions.

Many empirical models have been already developed in literature to interpret and investigate the Pd-based membrane behaviour.

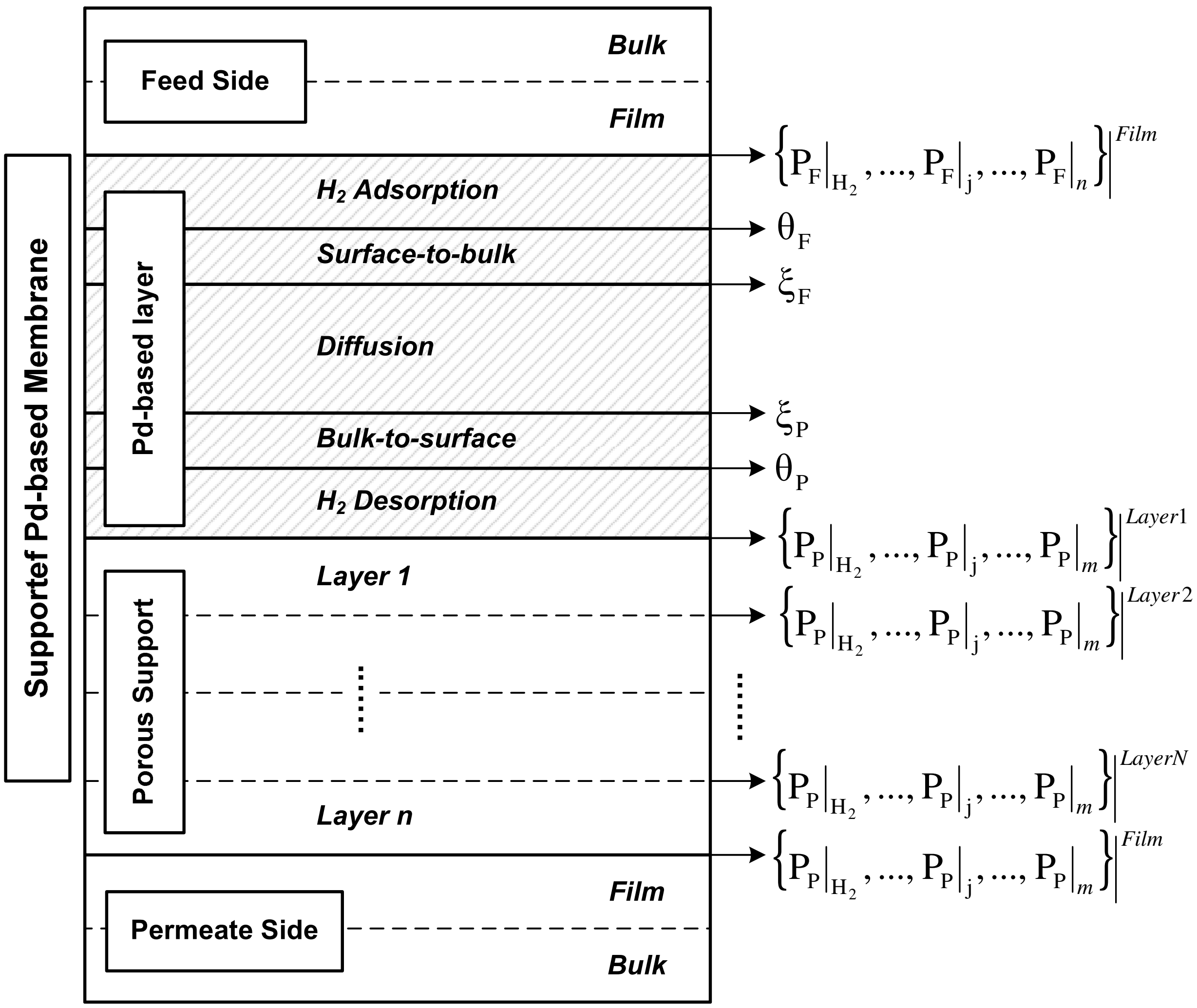
Nevertheless, systematic approaches to model the complex transport and kinetic phenomena regarding these membranes, evaluating also the concentration polarization influence, are still missing or inadequate.

Description of the permeation model

Model based on a multicomponent approach



Mathematical details of the model



$P_F|_j$ = **Partial pressure of the j^th^ species – Feed side**

θ = **Surface degree covered by atomic H, $mol_H\ mol_{Pd}^{-1}$**

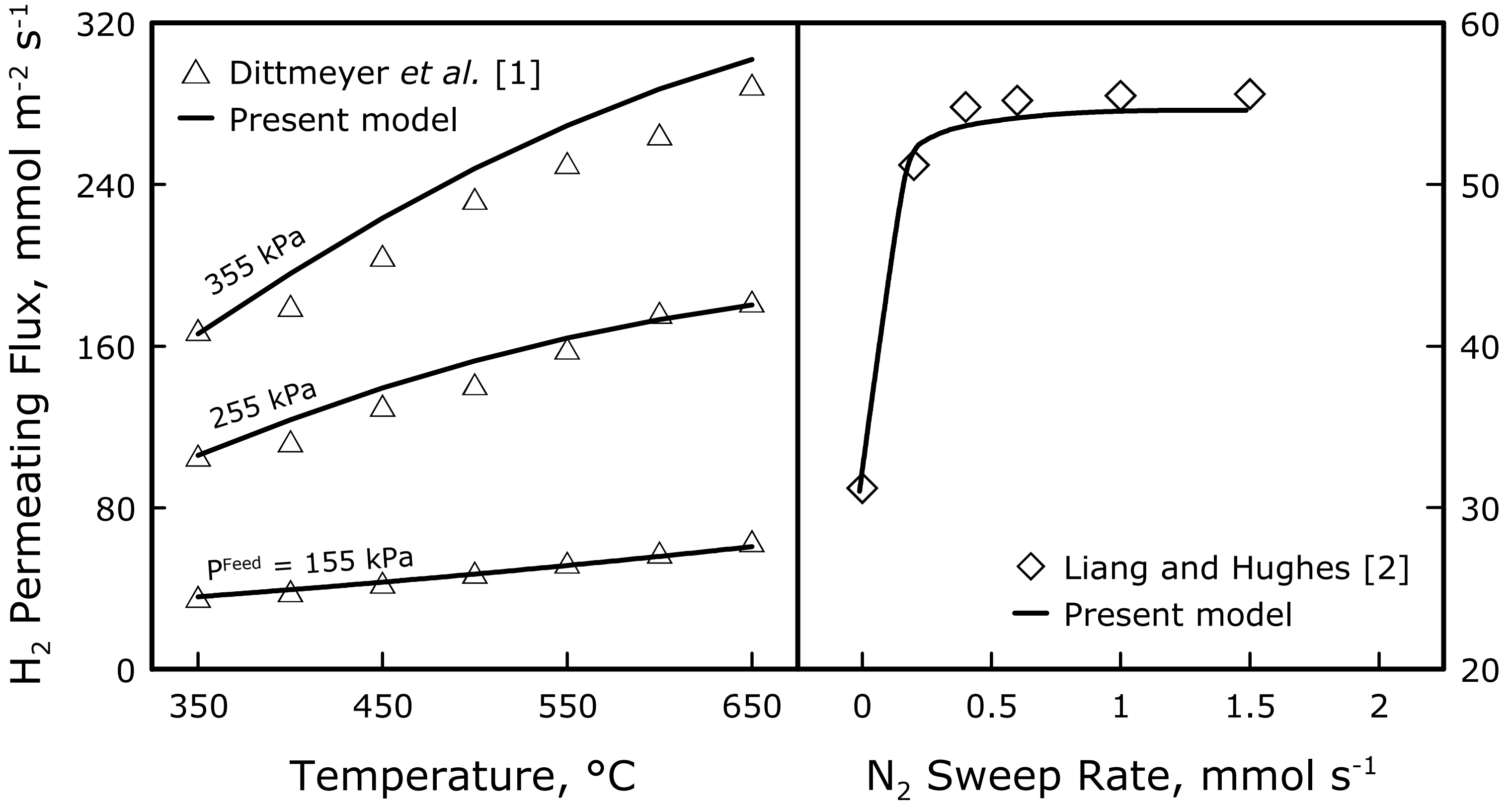
ξ = **Atomic H concentration inside the Pd-based lattice**

Each step is modelled by its own equations, which provide the value of the overall permeating flux as well as the H_2 profile through the membrane

Mathematical details of the model

Permeation Step	Flux Equation
Adsorption	$J_{\mathrm{H_2}}^{\mathrm{Ads}} = \dfrac{S_0\, F(\theta_\mathrm{F})}{\sqrt{2\pi \mathrm{M_{H_2}} RT}} \mathrm{P_F}\Big\rvert_{\mathrm{H_2}} - N_S^2 k_{Des}^0 \exp\left(-\dfrac{2E_{Des}}{RT}\right)\theta_\mathrm{F} G(\theta_\mathrm{F})$
Desorption	$J_{\mathrm{H_2}}^{\mathrm{Des}} = N_S^2 k_{Des}^0 \exp\left(-\dfrac{2E_{Des}}{RT}\right)\theta_\mathrm{P} G(\theta_\mathrm{P}) - \dfrac{S_0\, F(\theta_\mathrm{P})}{\sqrt{2\pi \mathrm{M_{H_2}} RT}} \mathrm{P_P}\Big\rvert_{\mathrm{H_2}}$
Diffusion	$J_{\mathrm{H_2}}^{Diff} = \dfrac{N_b}{2\delta^{Mem}} D_\mathrm{H}^0 \exp\left(-\dfrac{E_{Diff}}{RT}\right)\left[(\xi_\mathrm{F} - \xi_\mathrm{P}) + \left(\dfrac{1}{2} + \dfrac{b}{T}\right)(\xi_\mathrm{F}^2 - \xi_\mathrm{P}^2)\right]$
Surface-to-Bulk	$J_{\mathrm{H_2}}^{SB} = \dfrac{N_S\, \lambda_{j0}}{6}\left[(1-\xi_\mathrm{F})\dfrac{T^{0.25}}{c_1}\exp\left(-\dfrac{E_{SB}}{RT}\right)\sqrt{\dfrac{G(\theta_\mathrm{F})\theta_\mathrm{F}}{F(\theta_\mathrm{F})}} - \xi_\mathrm{F}\exp\left(-\dfrac{E_{BS}}{RT}\right)\right]$
Bulk-to-Surface	$J_{\mathrm{H_2}}^{BS} = \dfrac{N_S\, \lambda_{j0}}{6}\left[\xi_\mathrm{P}\exp\left(-\dfrac{E_{BS}}{RT}\right) - (1-\xi_\mathrm{P})\dfrac{T^{0.25}}{c_1}\exp\left(-\dfrac{E_{SB}}{RT}\right)\sqrt{\dfrac{G(\theta_\mathrm{P})\theta_\mathrm{P}}{F(\theta_\mathrm{P})}}\right]$
Mass transfer in film on Feed and Permeate side (Multicomponent film theory)	$\vec{N} = \dfrac{1}{RT}\{Kc\}\cdot\{Z\}\cdot\left(\vec{P}^{Bulk} - \vec{P}^{Surface}\right) + \dfrac{N_{Total}}{P_{Total}}\vec{P}^{Surface}$
Mass transfer in each layer of the porous support (Dusty Gas Model)	$\sum_{j=1}^{n}\dfrac{x_j N_i - x_i N_j}{C_{Total}\, D_{ij,effective}^{MaxwellStefan}} + \dfrac{N_i}{C_{Total}\, D_{i,effective}^{Knudsen}} = -\nabla x_i - \dfrac{x_i \overline{\mathrm{V}}_i}{RT}\nabla P - x_i\dfrac{B_0}{\eta\, D_{i,effective}^{Knudsen}}\nabla P$

Model validation with data from literature



A good accordance between model and experimental data is found for two supported membranes in several conditions.

[1] Dittmeyer et al., 2001. *J. Mol. Cat. A: Chem.*, 173: 135-184.   [2] Liang and Hughes, 2005. *Chem. Eng. J.*, 112: 81-86.

Operating conditions

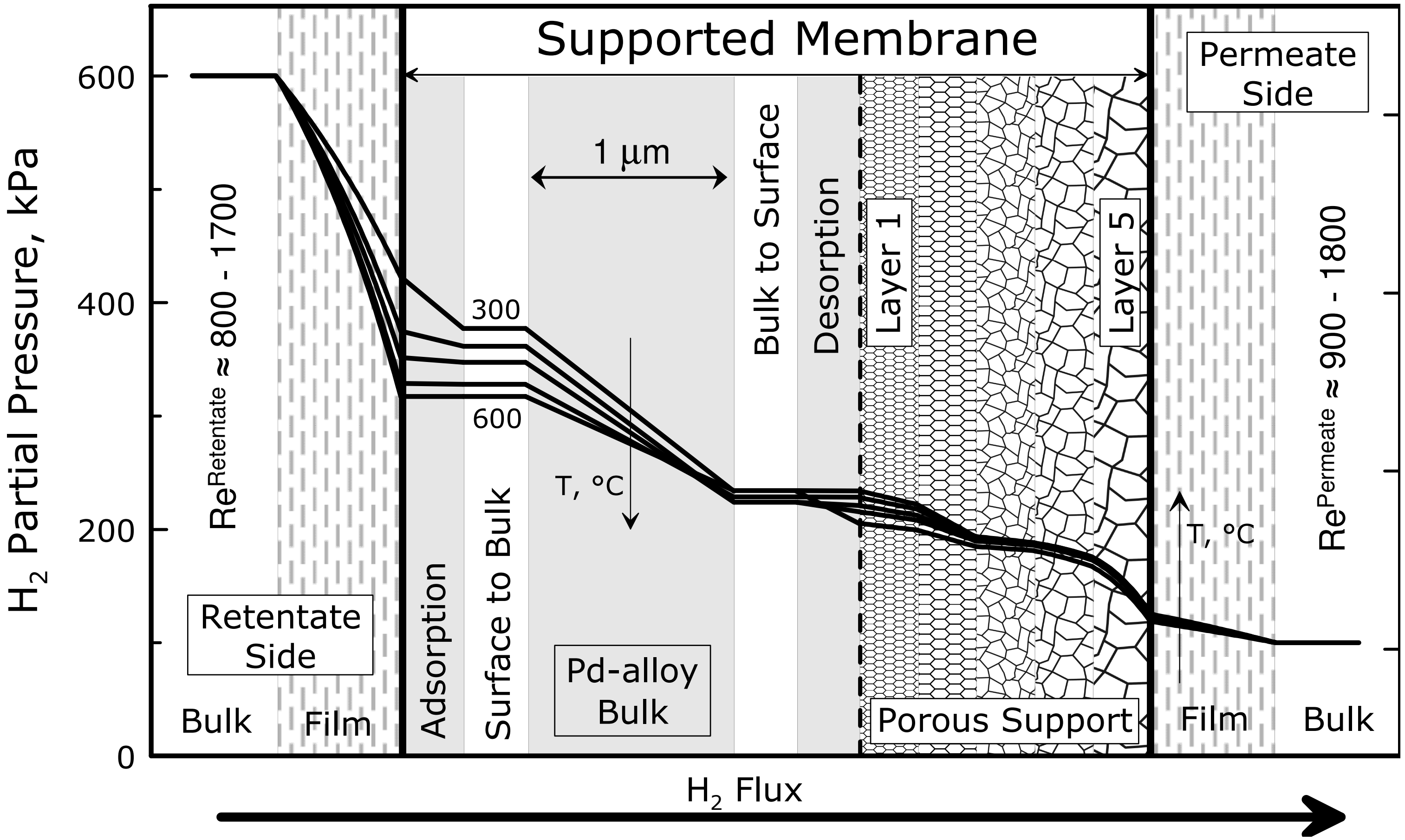
Side	Pressure, kPa							Reynolds number, -
	H_2	CH_4	CO_2	H_2O	CO	N_2	Total	
Retentate	600	75	50	50	25	75	875	1700 - 800* 4000 - 2500**
Permeate	100	-	-	80	-	20	200	1800 - 900* 3000 - 4200**

Temperatures = [300 - 600]ºC

**Laminar flow conditions.* ***Turbulent flow conditions.*

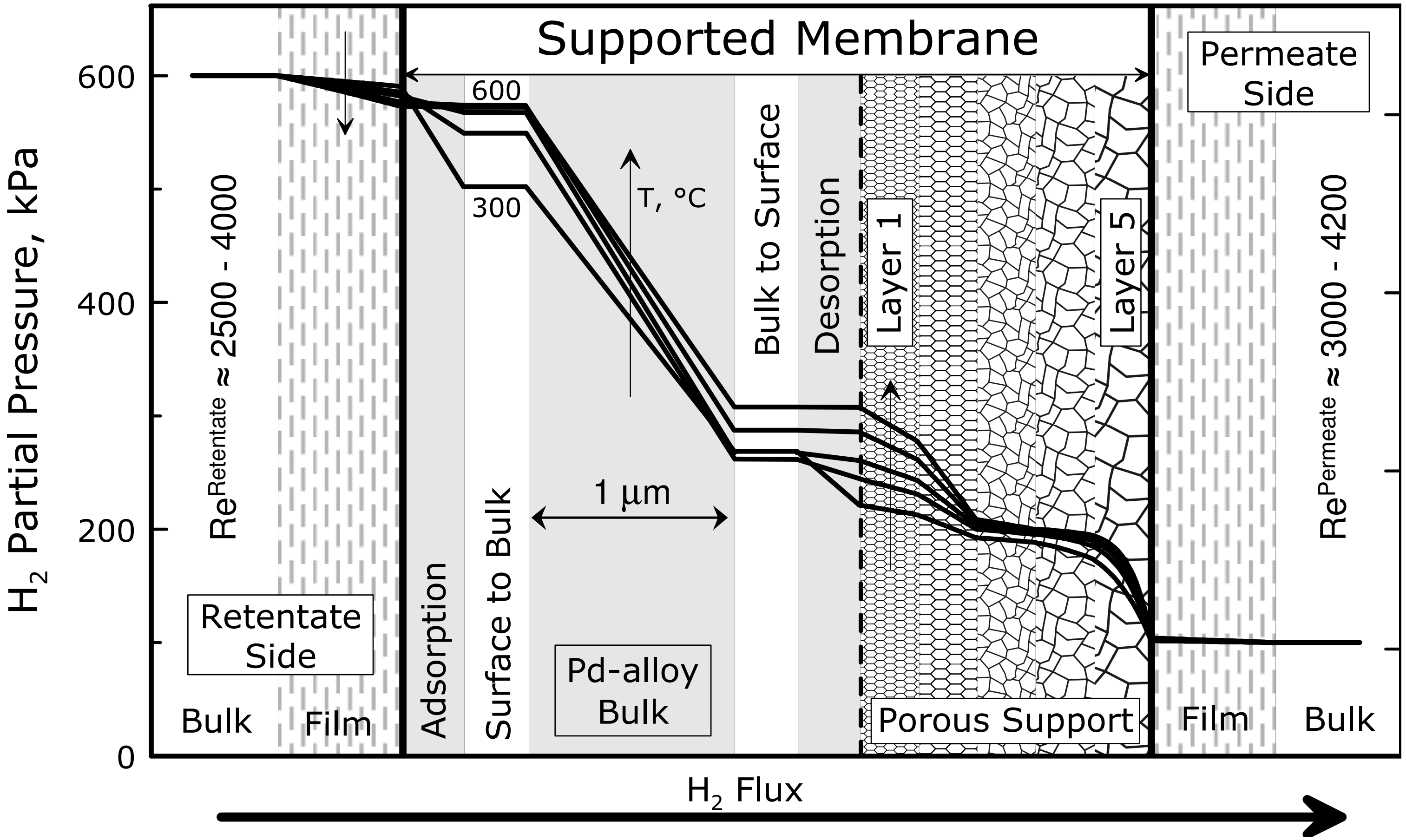
Multicomponent mixtures have been considered in both retentate and permeate side to reproduce a more real situation of separation process.

Transmembrane profiles – Laminar flow



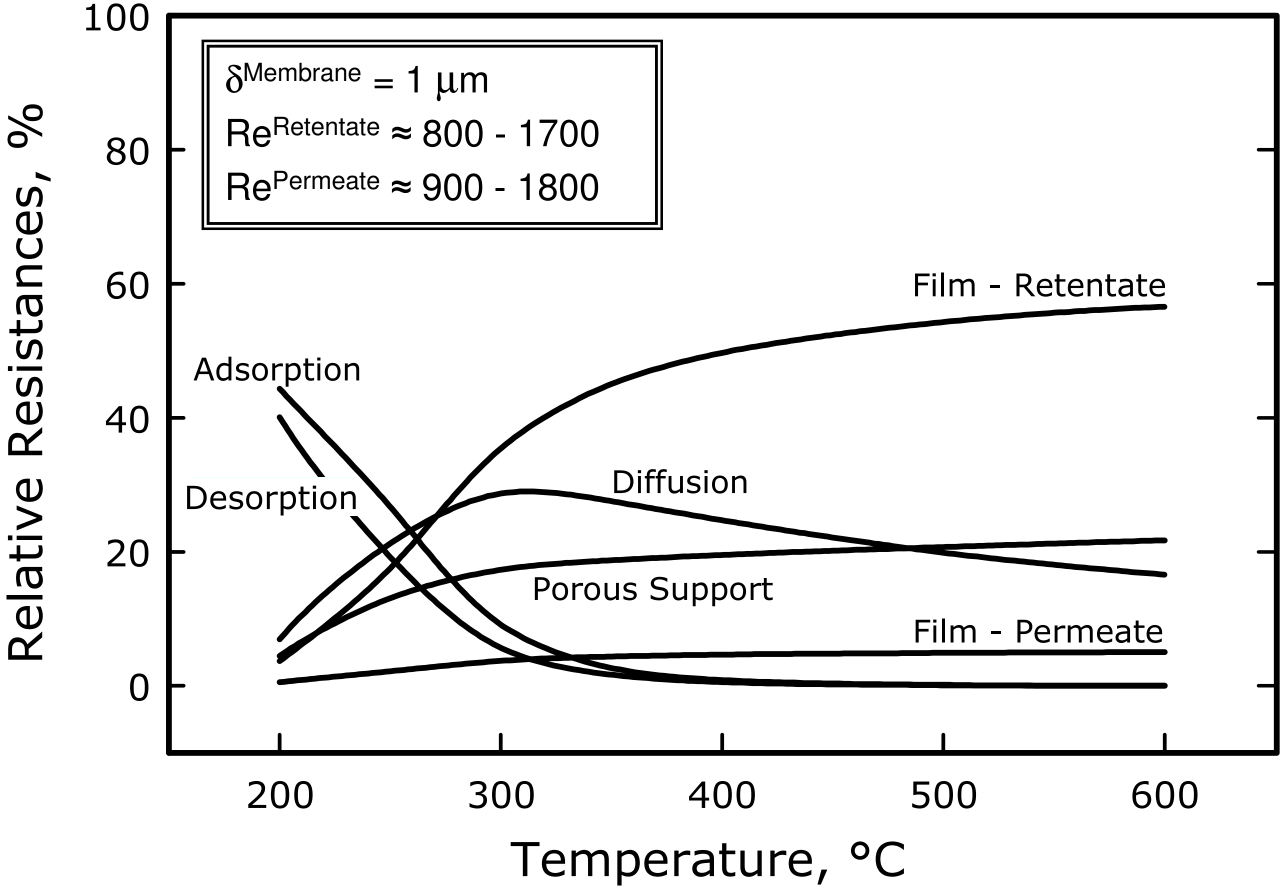
The model solution provides the H_2 flux value and the transmembrane H_2 partial pressure profiles as functions of the operating conditions.

Transmembrane profiles – Turbulent flow



The variables θ and ξ on the membrane surface and inside the lattice, respectively, are expressed in form of equivalent H_2 partial pressures.

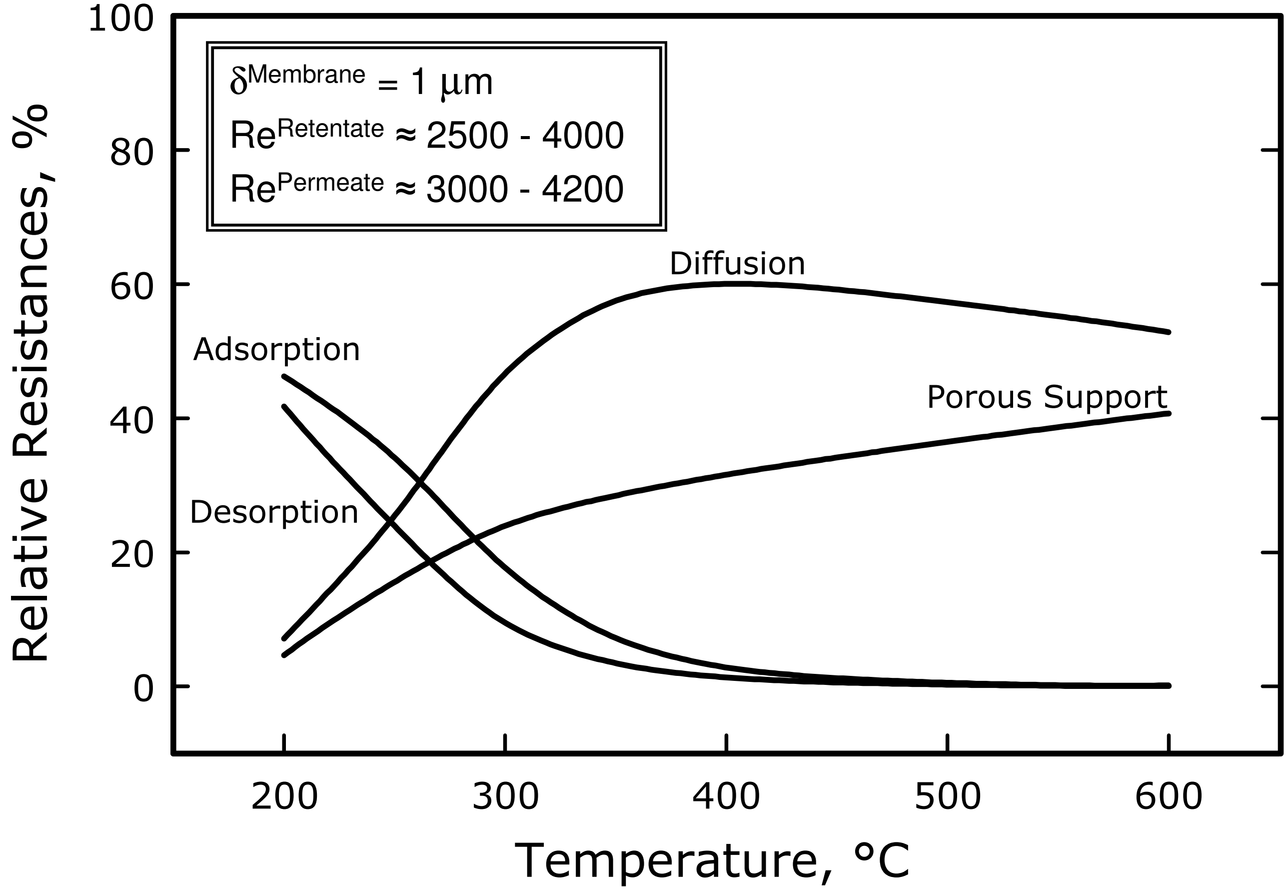
Step resistances to flux – Laminar flow



$$R.R. \equiv \frac{\Delta P_{H_2}^{Step\,j}}{\Delta P_{H_2}^{Tot}}$$

In laminar conditions, the influence of the external mass transfer can be relevant.

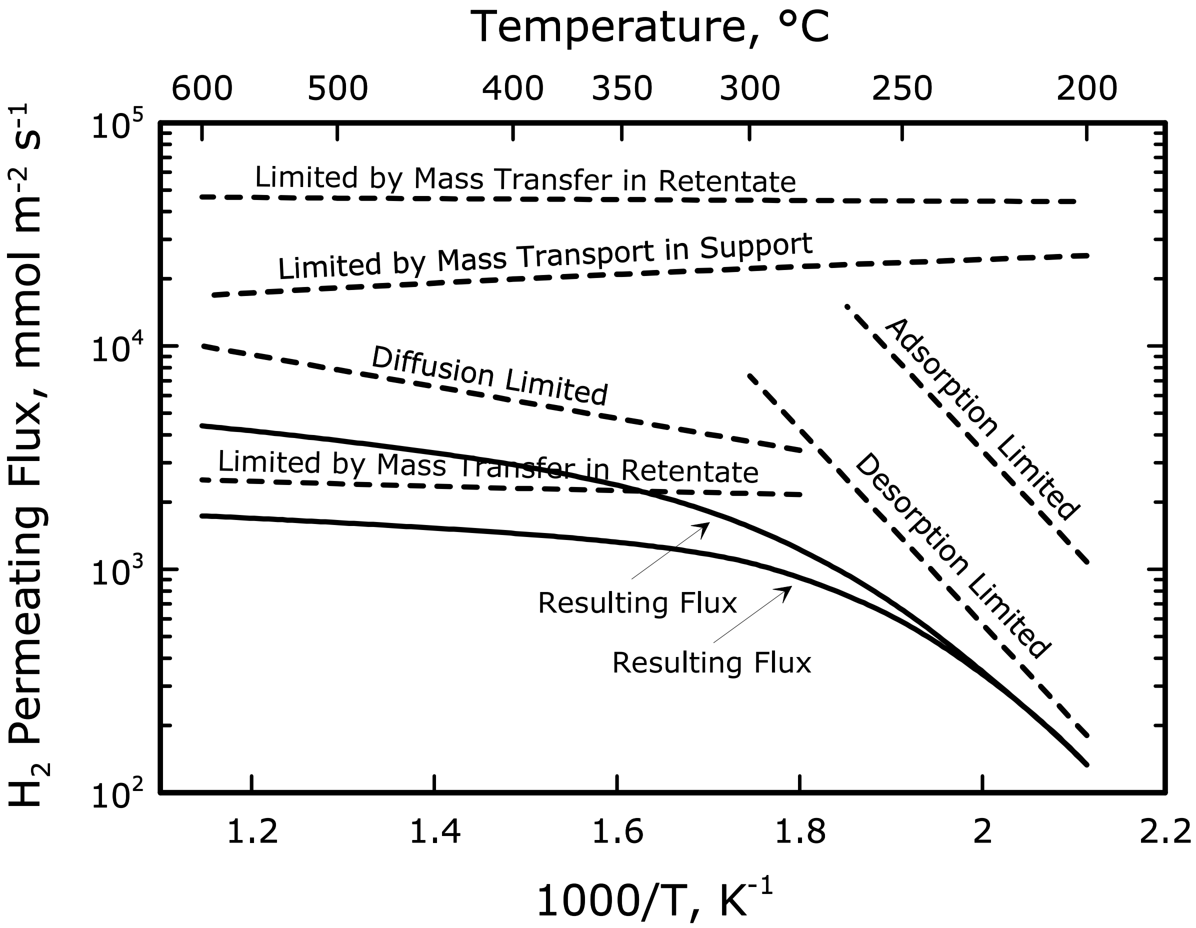
Step resistances to flux – Turbulent flow



$$R.R. \equiv \frac{\Delta P_{H_2}^{Step\,j}}{\Delta P_{H_2}^{Tot}}$$

In turbulent conditions, only four steps influences the overall permeation process.

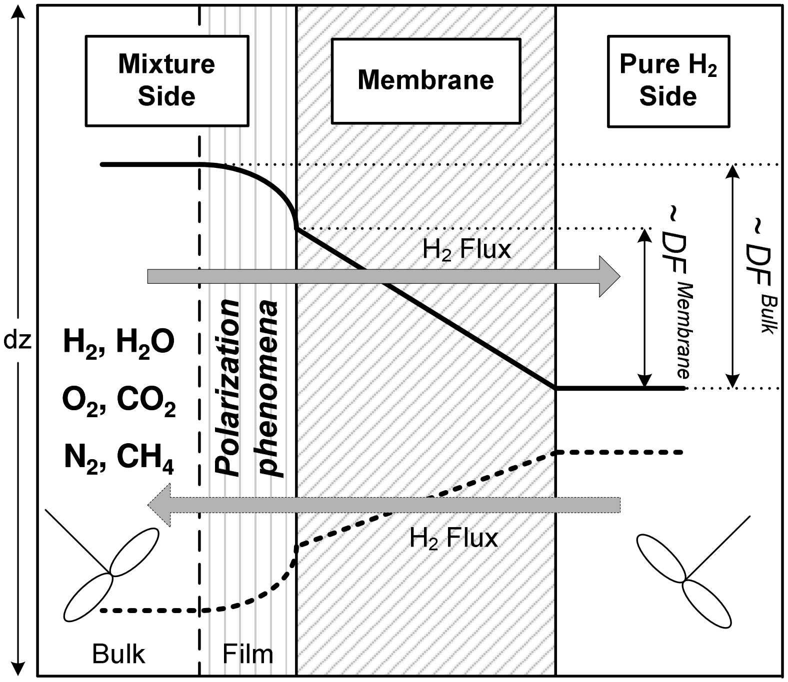
Flux vs. T – Laminar and Turbulent flow



The overall flux can be seen as the results of a complex combination of all the limiting fluxes related to the elementary steps considered.

Depending on the operating conditions, the flux tends to follow the behaviour of the most influencing step.

Evaluation of the Concentration Polarization



The quantities π^{Mem} and DF^{Bulk} are directly evaluable from pure H_2 test and from the external operating conditions, respectively.

$$\mathrm{H_2\ Flux(Elementary\ Steps)} = \pi^{Bulk}\, DF^{Bulk} = (1-CPC)\, \pi^{Membrane}\, DF^{Bulk}$$

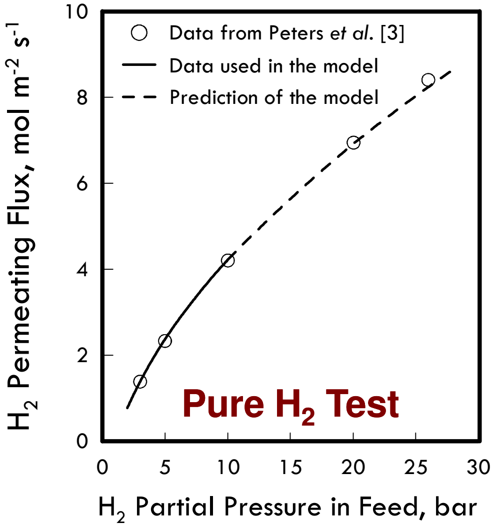
$$CPC = 1 - \frac{\mathrm{H_2\ Flux(Elementary\ Steps)}}{\pi^{Membrane}\, DF^{Bulk}}$$

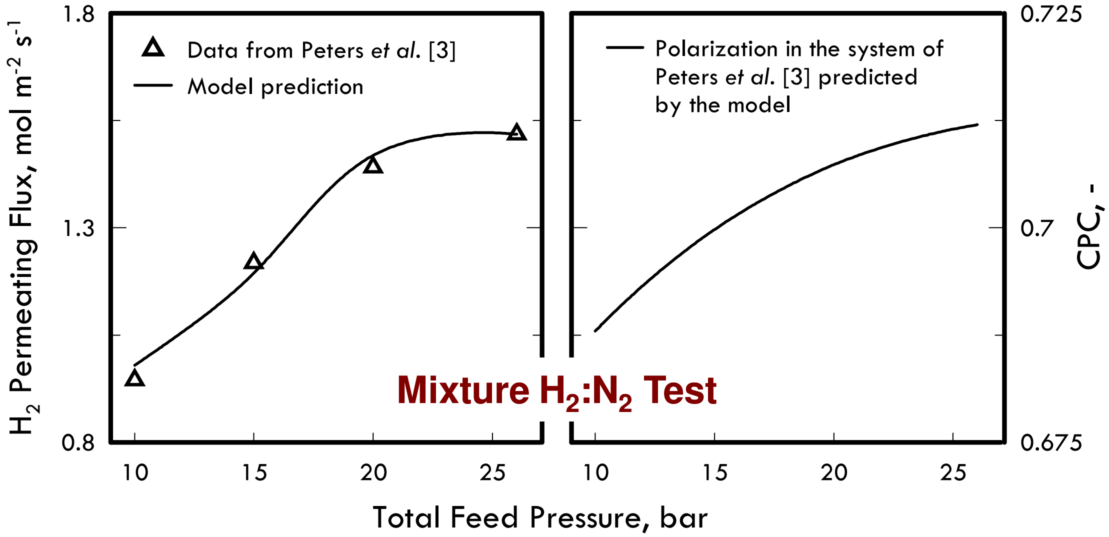
$$DF \equiv DF^{Sieverts} \equiv \Delta\sqrt{\mathrm{P_{H_2}}} = \left(\sqrt{\mathrm{P}_{\mathrm{H_2}}^{Upstream}} - \sqrt{\mathrm{P}_{\mathrm{H_2}}^{Downstream}}\right)$$

$$CPC = 1 - \frac{\mathrm{H_2\ Flux(Elementary\ Steps)}}{\pi^{Membrane}\, \Delta\sqrt{\mathrm{P_{H_2}}}\Big|^{Bulk}}$$

$$CPC = 1 - \frac{DF^{Mem}}{DF^{Bulk}} = 1 - \frac{\pi^{Bulk}}{\pi^{Mem}} \rightarrow \begin{cases} 0, & \text{No Polarization} \\ 1, & \text{Maximum Polarization} \end{cases}$$

Concentration polarization analysis





Test type	Conditions
Pure H_2 in both membrane sides	$\delta^{Membrane}$ = 2.2 µm T = 400 °C
Concentration Polarization Case (Feed: Binary mixture H_2:N_2 at 50:50) Permeate: Sweep of pure N_2	P^{Feed} = [3, ..., 26] bar $P^{Permeate}$ = 1.01 bar

[3] Peters T.A. *et al.*, 2008. *J. Mem. Sci.*, 316: 119-127.

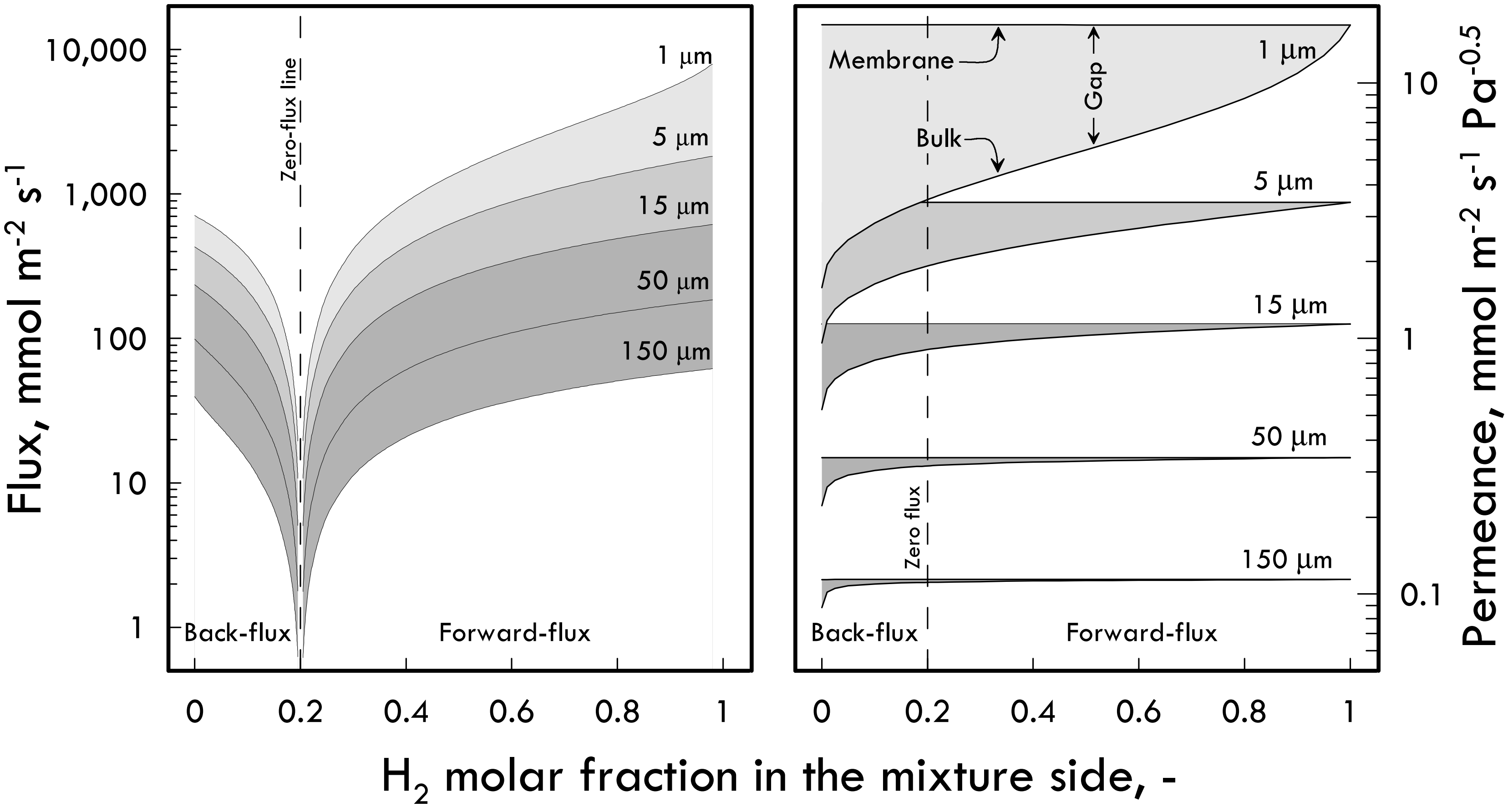
Polarization analysis - Operating conditions

Side	*Molar fraction, -*						*Total pressure, kPa*	*Reynolds number, -*
	H_2	CH_4	CO_2	H_2O	O_2	N_2		
Mixture	{0 ... 1}	{0.2 ... 0} for each species					{100 ... 1000}	2100 - 8000
Pure H_2	1	Absent					{100 ... 800}	Not influent

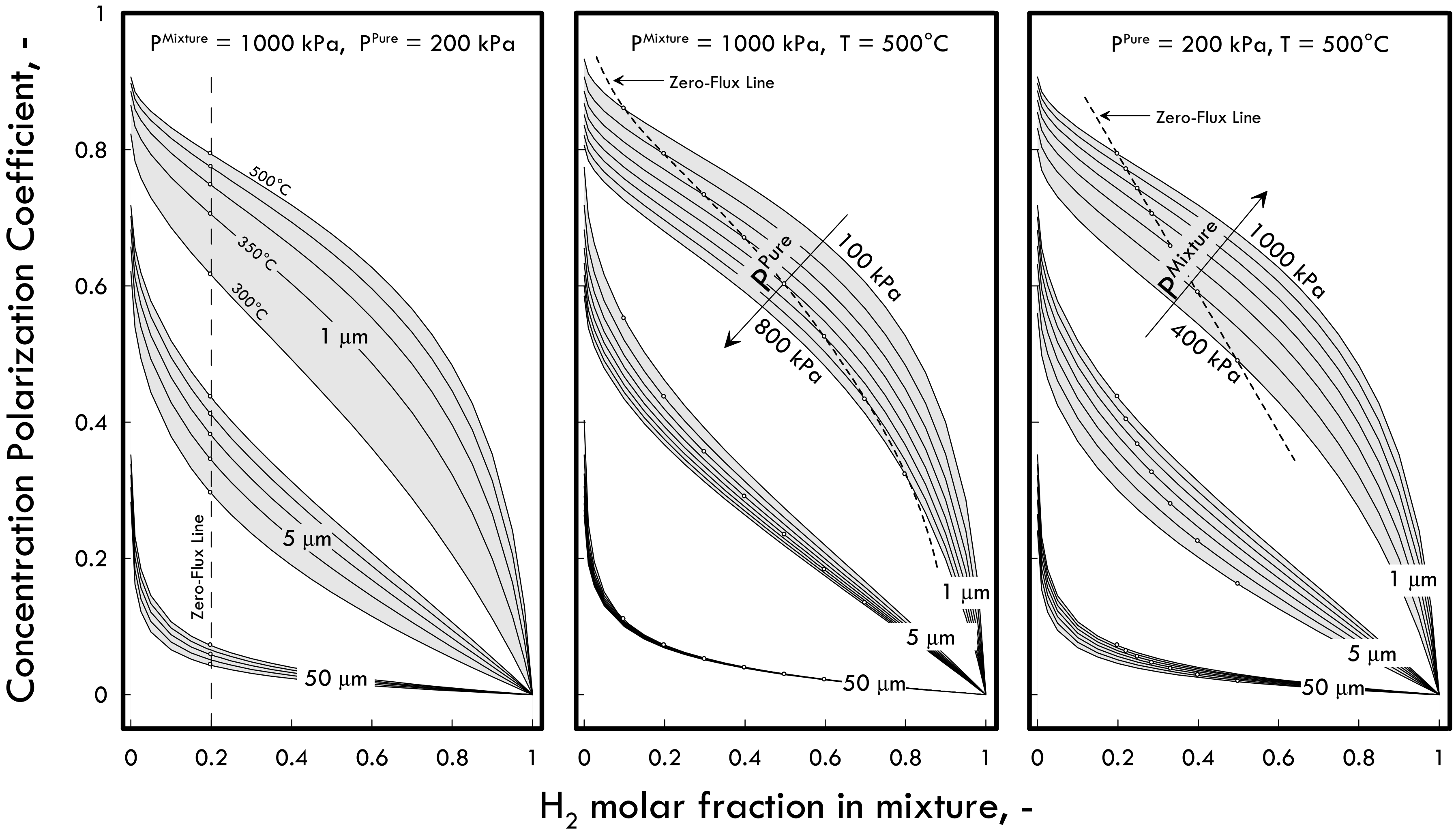
Temperatures = [300 - 500]ºC

Flux and permeance vs. x_{H_2}

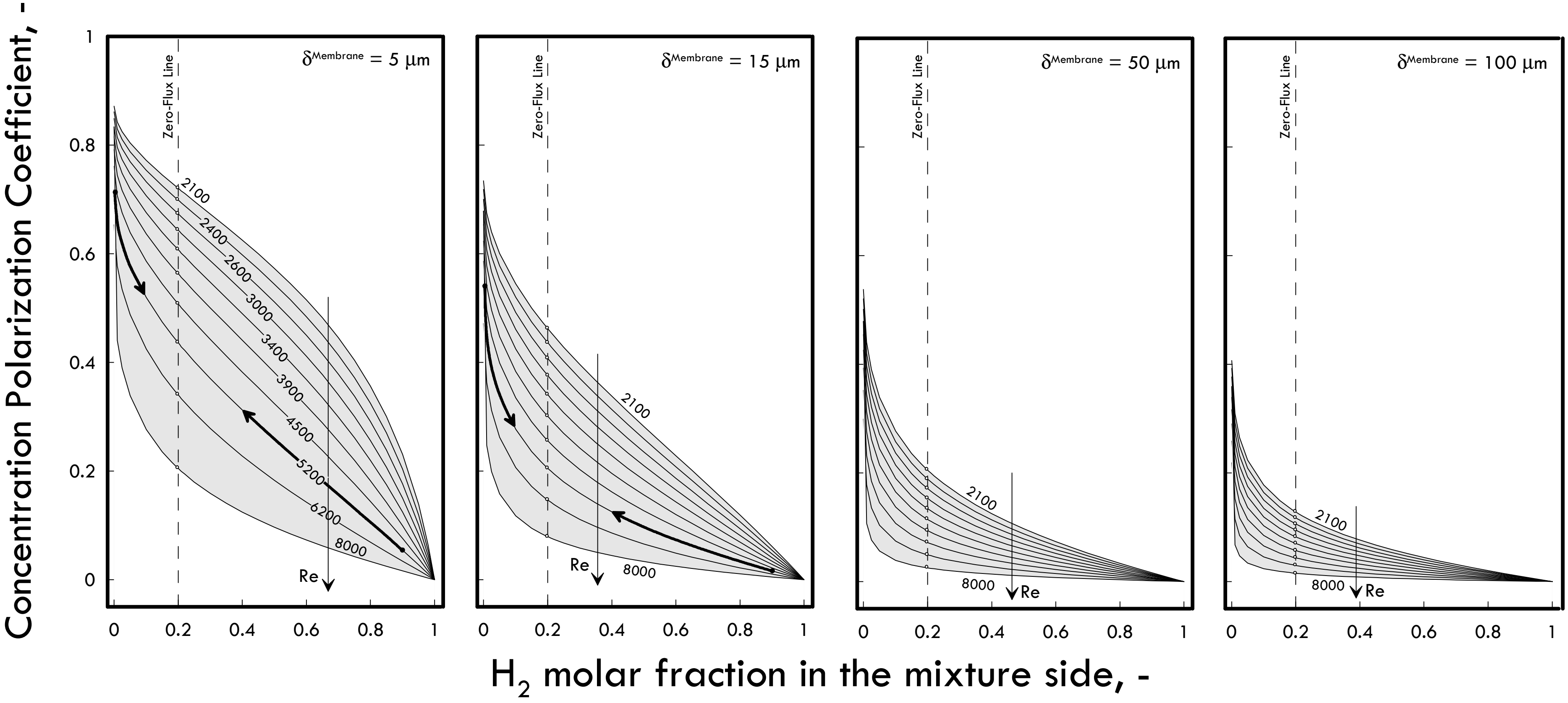
$P^{Mixture} = 1000$ kPa, $P^{Pure} = 200$ kPa, T = 500 °C, Re @ 5200



Polarization maps – CPC vs. x_{H_2}



Polarization maps – CPC vs. x_{H_2}



The influence of the concentration polarization significantly decreases as high membrane thicknesses are considered, because the diffusion in the Pd-based bulk progressively tends to become the only rate-determining step.

Overall Conclusions

- ❑ **A new model for H_2 permeation through supported Pd-based membranes was developed, accounting for several elementary steps.**
  - ✓ **The model predictions were compared with some experimental data, showing a good agreement with them.**
  - ✓ **The rate determining steps were identified as functions of temperature, membrane thickness and fluid-dynamic conditions.**
  - ✓ **The overall permeating flux has been evaluated as a function of the limiting fluxes of all the elementary steps considered.**
- ❑ **A systematic analysis was provided for the concentration polarization in self-supported Pd-based membranes by modifying the original Sieverts' law.**
  - ✓ **The effect of the concentration polarization has been evaluated by means of an appropriately defined Concentration Polarization Coefficient CPC.**
  - ✓ **CPC has been calculated as a function of several conditions (temperature, membrane thickness, feed and permeate pressure, and Reynolds' number) in order to better predict the hydrogen flux.**

Thanks for Your Kind Attention