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

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Concentration polarization present in any membrane separation affects the system performance depending on the membrane permeance, i.e., a higher permeance leads to a higher polarization. Hydrogen transport in Pd-based supported membranes was described by means of a model [1] considering several elementary steps of the permeation process, improving what done by Ward and Dao for self-supported membranes. The model includes the external mass transfer in the multicomponent gaseous phases on both membrane sides, described by the Stefan-Maxwell equations. The transport of the multicomponent mixture in the multilayered porous support was also considered and described by means of the Dusty Gas Model, which takes into account Knudsen, Poiseuille and ordinary diffusion. The diffusion in the Pd-alloy layer is modeled by taking the hydrogen chemical potential as the driving force of the diffusion in the metallic bulk. The interfacial phenomena (adsorption, desorption, transition from Pd-based surface to Pd-based bulk and vice-versa) were described by the same expressions used by Ward and Dao. The model separates the permeation steps and consequently their influence, quantifying the relative resistances offered by each of them. Comparison with some experimental literature data shows a good agreement. The developed tool is able to describe hydrogen transport through a supported Pd-based membrane, recognizing the rate determining steps (e.g., diffusion in the metallic bulk or in the porous support) involved in the permeation.

The concentration polarization coefficient was evaluated by an opportune coefficient[2] expressed as a function of the ratio of the flux calculated by means of this new validated complex model and the one obtained by the Sieverts' law utilizing the bulk driving force and hydrogen permeance. It was evaluated as a function of several operating conditions: up-stream hydrogen molar fraction ([0...1]), total pressure of upstream ([200,...,1000] kPa), total pressure of down-stream ([100,...,800] kPa), temperature ([300,...,500]°C), membrane thickness ([1,...,150] μm), permeance ([0.1,...,20] mmol m^{-2} s^{-1} $Pa^{-0.5}$) and upstream fluid-dynamic conditions (Reynolds' number).

The analysis shows that the polarization effect can be relevant not only when using very thin membranes (1 - 5 μm ca.), but also when thicker ones (100 μm ca.) are operated in specific conditions. The so-called "polarization maps", on which the influence of concentration polarization can be evaluated quantitatively in different conditions, provide concentration polarization coefficient in several operating conditions.

1) Caravella A., Barbieri G. and Drioli E., 2008. Modelling and Simulation of Hydrogen Permeation through Supported Pd-based Membranes with a Multicomponent Approach. Chemical Engineering Science, 63 (8), 2149-2160
2) Caravella A., Barbieri G. and Drioli E., 2009. Concentration polarization analysis in self-supported Pd-based membranes. Separation and Purification Technology, 66: 613-624

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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.

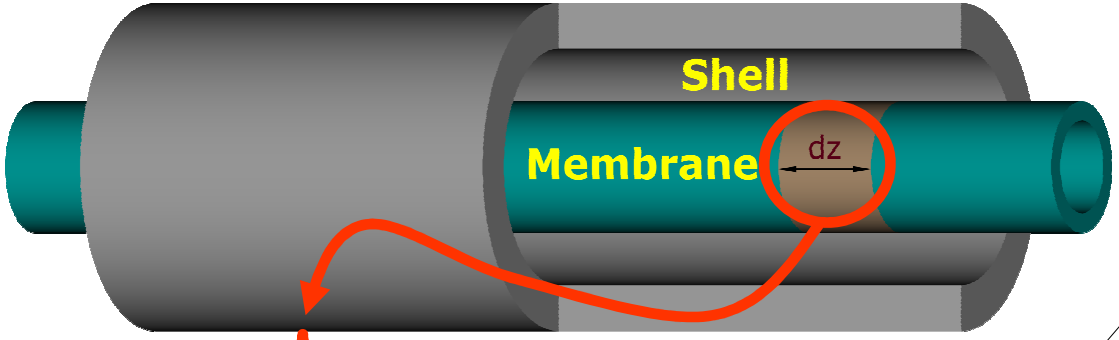
Hence, their integration in production and purification process could lead up to significant advantages with respect to traditional equipments.

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.

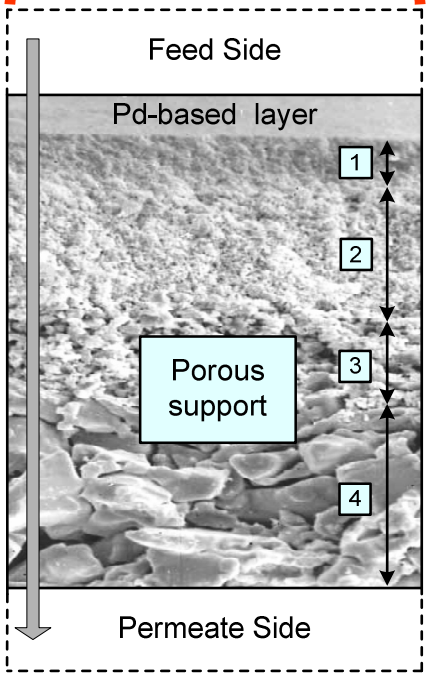
Nevertheless, systematic approaches to model the complex transport and kinetic phenomena regarding these membranes, evaluating also the concentration polarization influence, are still missing or inadequate.

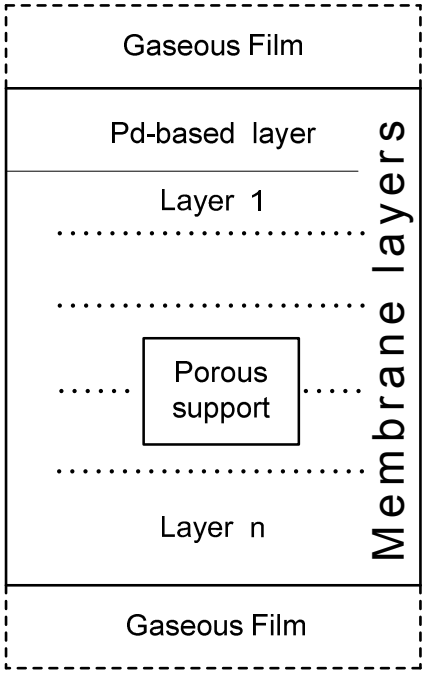
Description of the permeation model

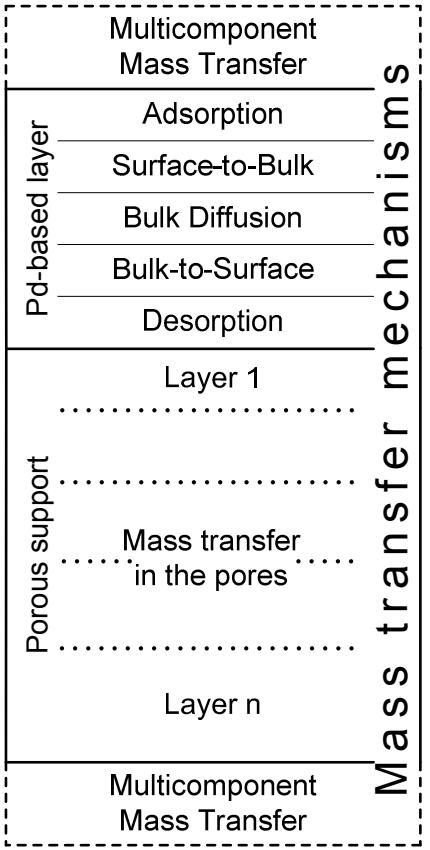


Model based on a multicomponent approach

Physical system

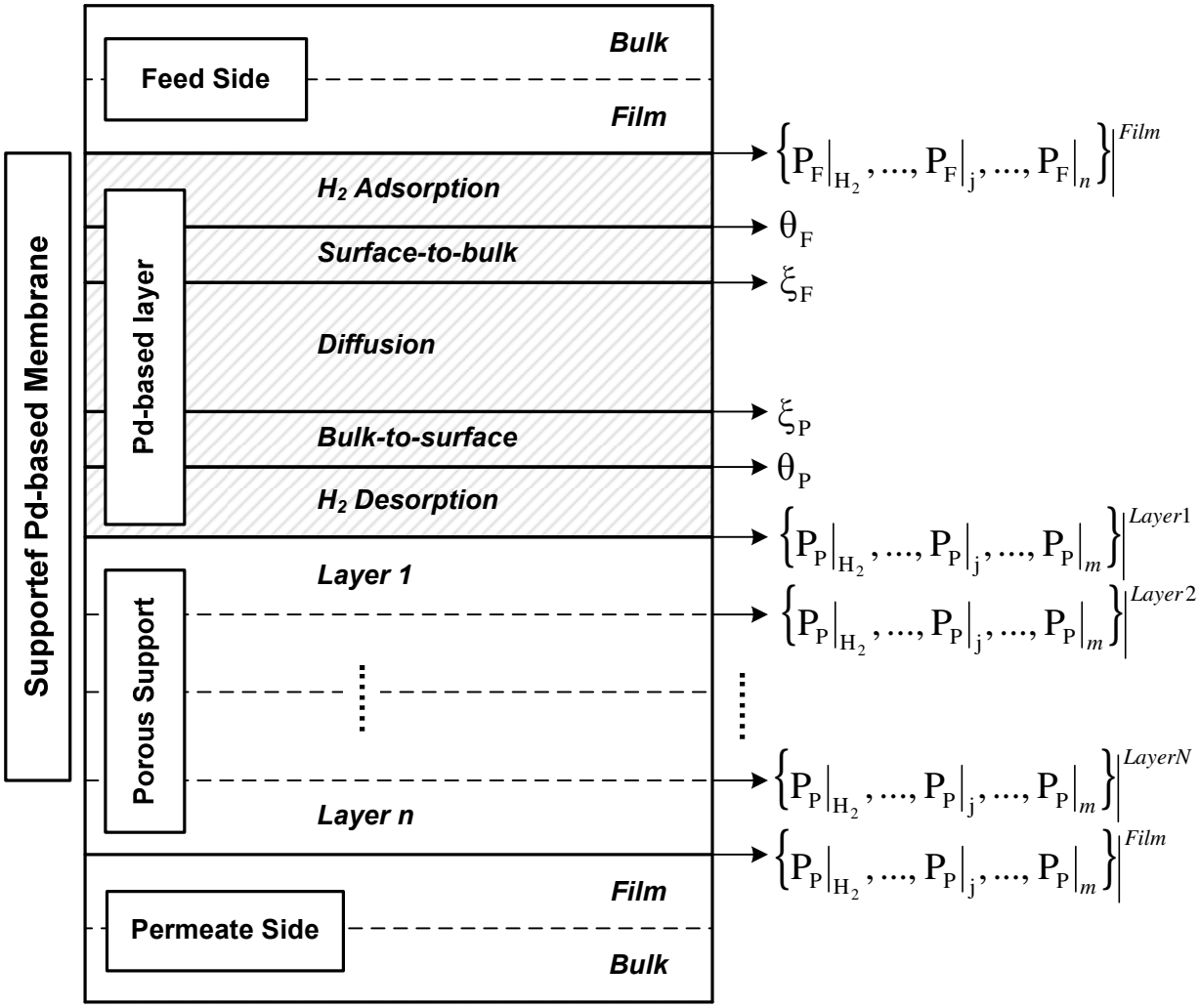






Mathematical description

Mathematical details of the model



$P_F|_j$ = Partial pressure of the jth species – Feed side

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

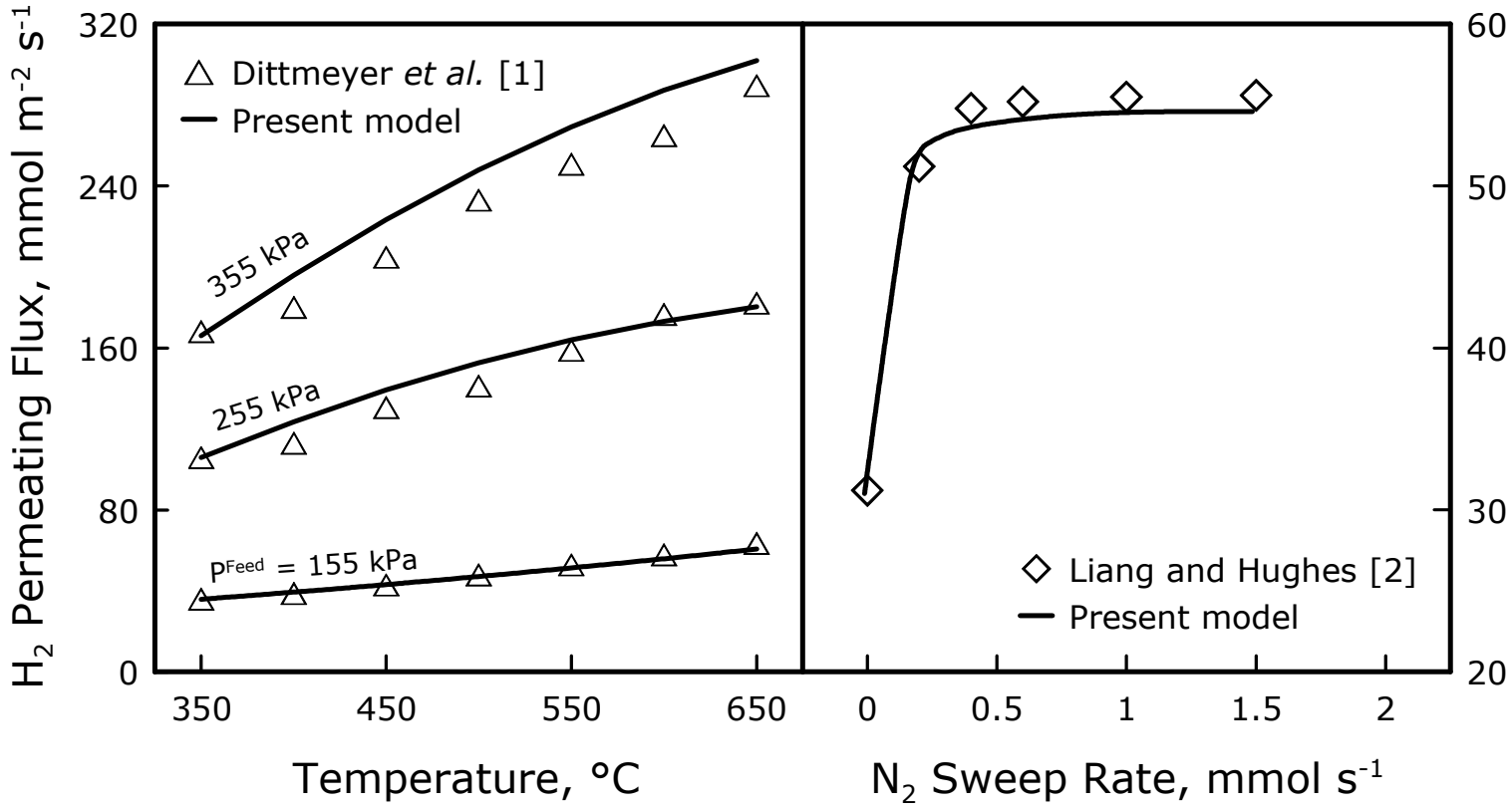
ξ = Atomic H concentration inside the Pd-based lattice

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

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

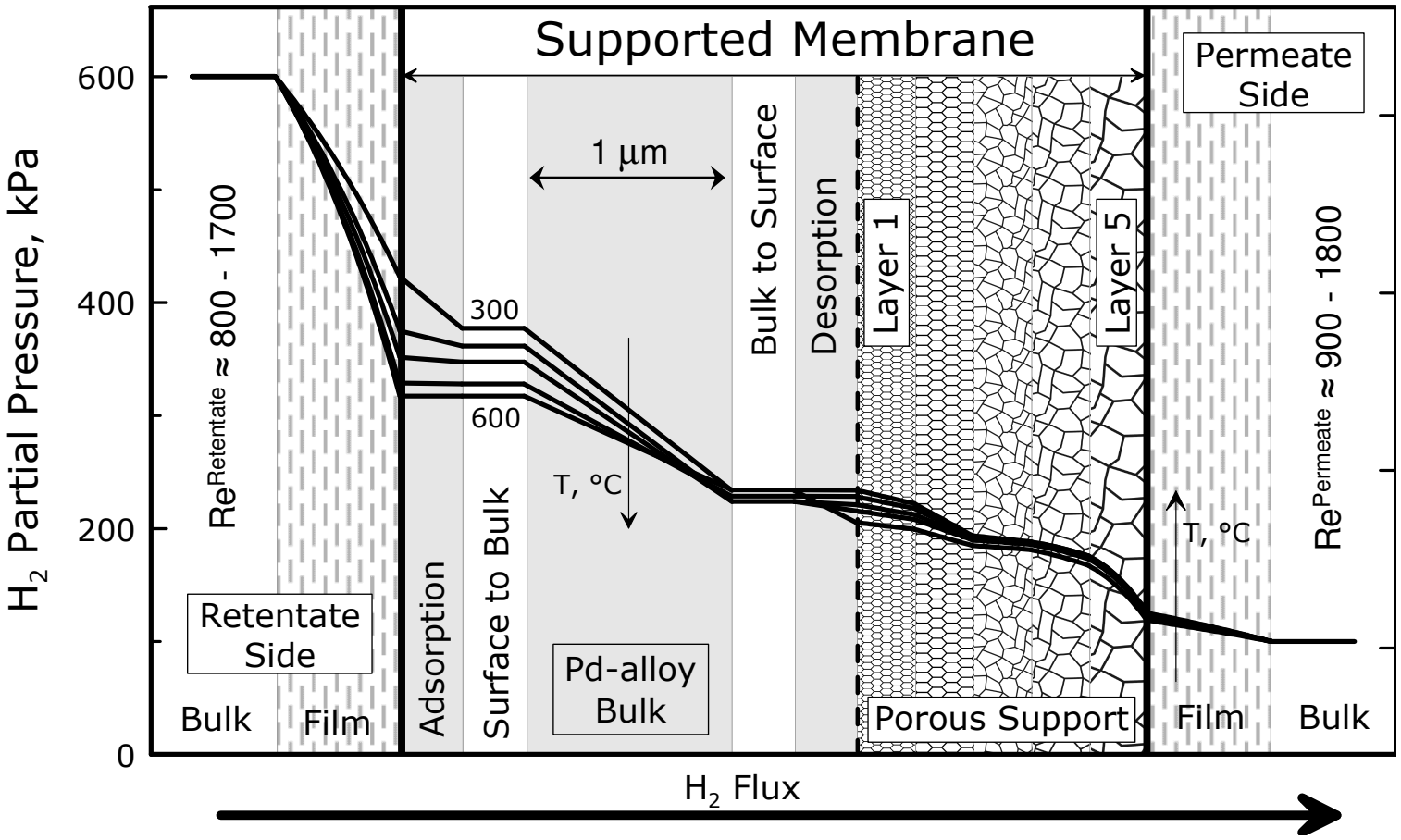
Side	Pressure, kPa							Reynolds number, -
	H_2	CH_4	CO_2	H_2O	CO	N_2	Total	
Retentate	600	75	50	50	25	75	875	1700 - 800* 4000 - 2500**
Permeate	100	-	-	80	-	20	200	1800 - 900* 3000 - 4200**

Temperatures = [300 - 600]ºC

*Laminar flow conditions. **Turbulent flow conditions.

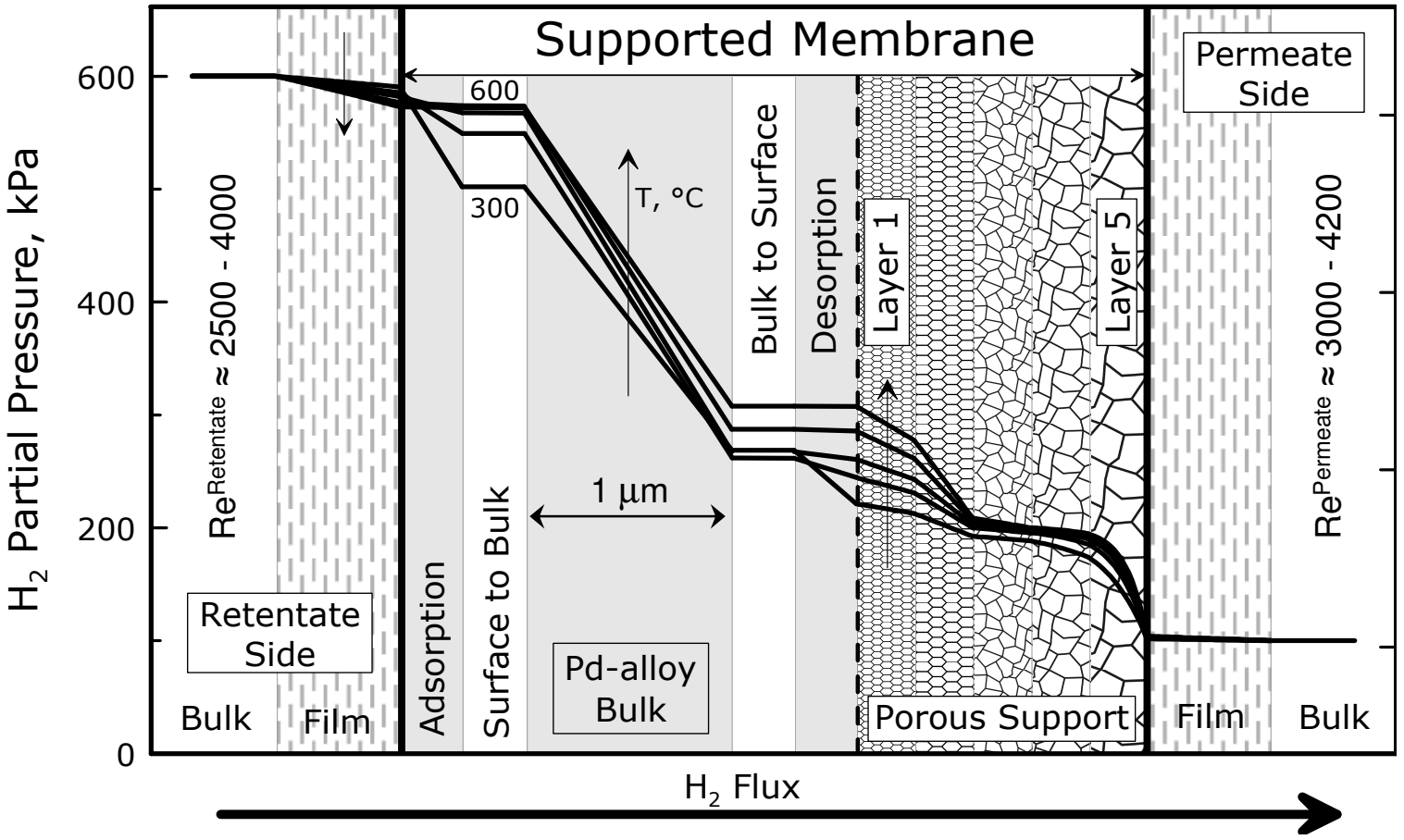
Multicomponent mixtures have been considered in both retentate and permeate side to reproduce a more real situation of separation process.

Transmembrane profiles – Laminar flow



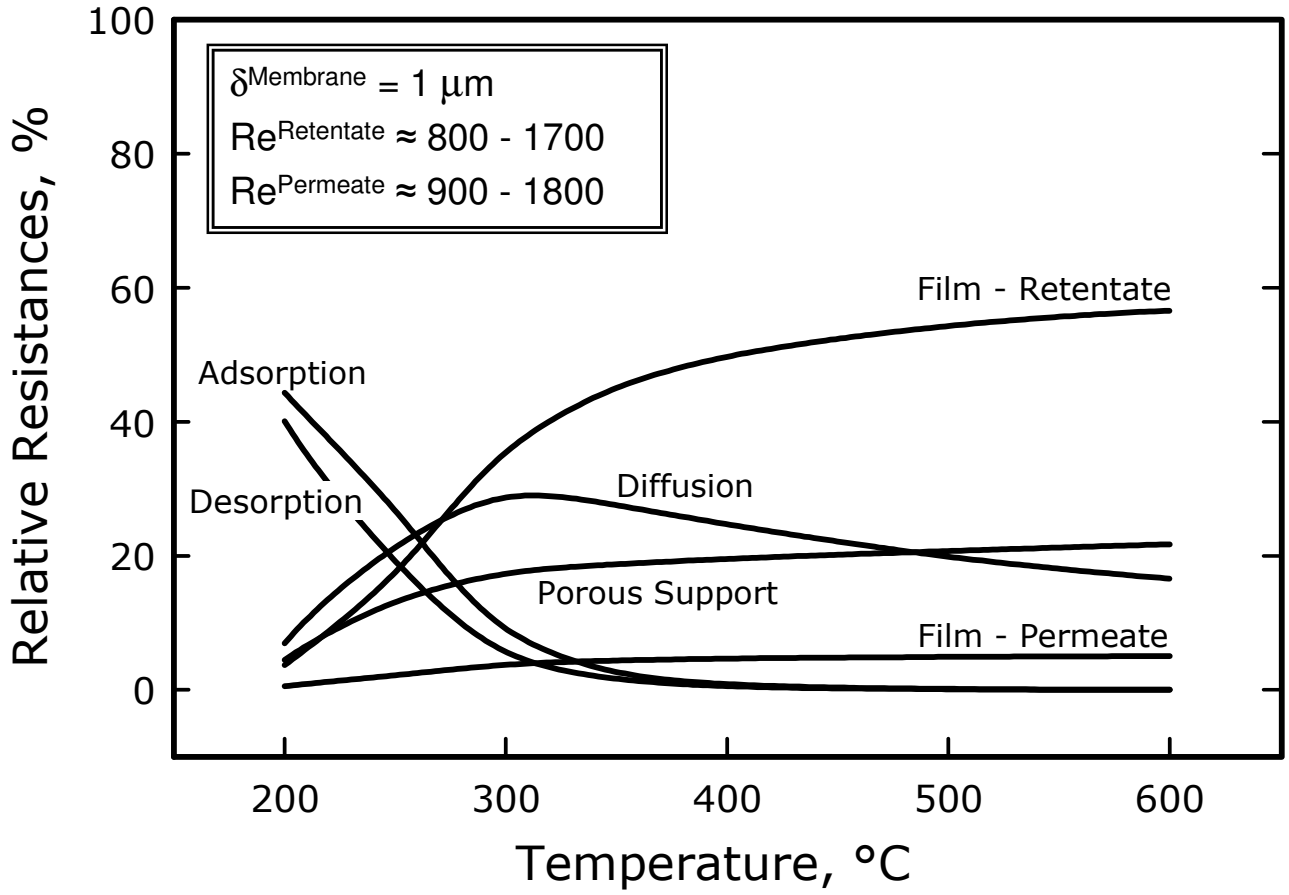
The model solution provides the H_2 flux value and the transmembrane H_2 partial pressure profiles as functions of the operating conditions.

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.

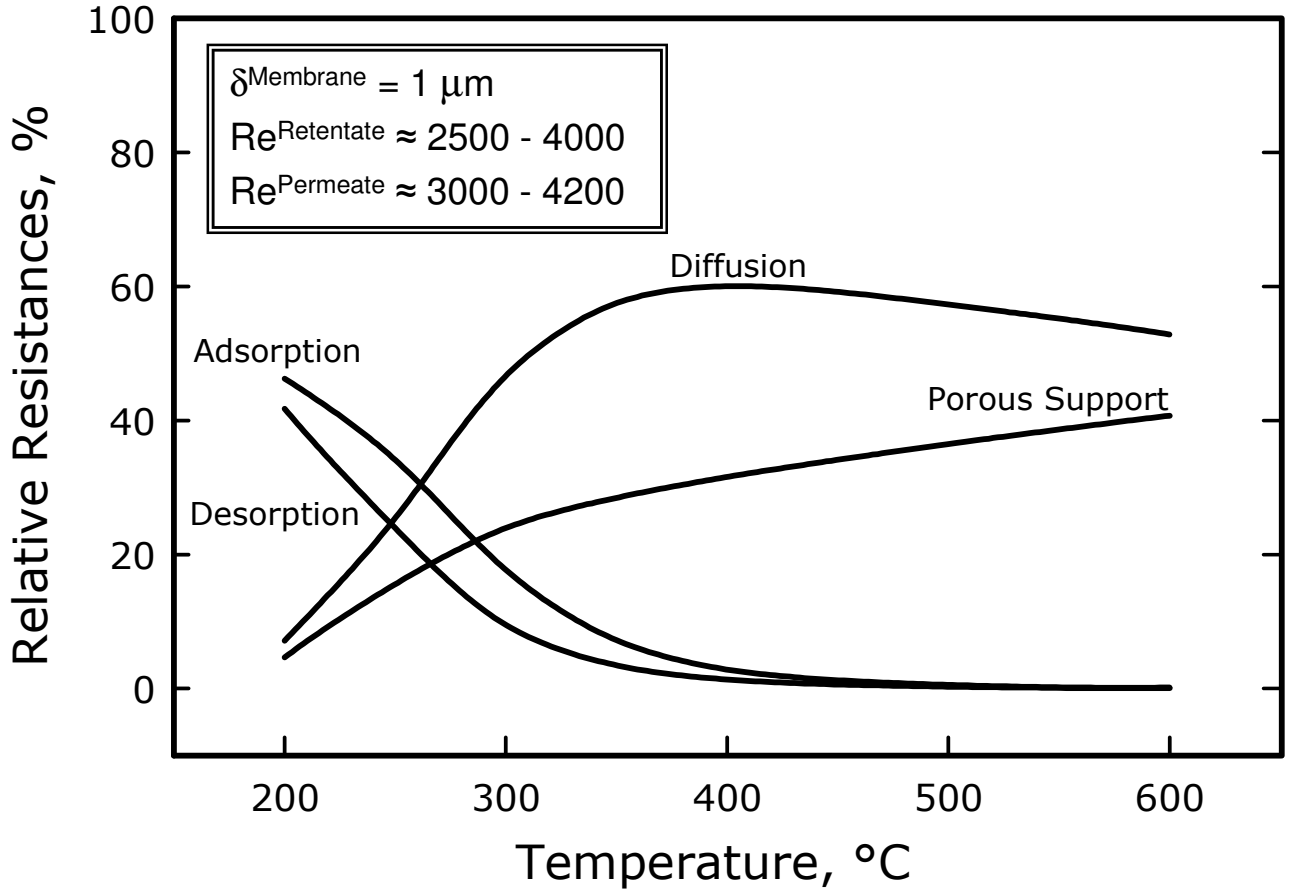
Step resistances to flux – Laminar flow



$$R.R. \equiv \frac{\Delta P_{H_2}^{Step_j}}{\Delta P_{H_2}^{Tot}}$$

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

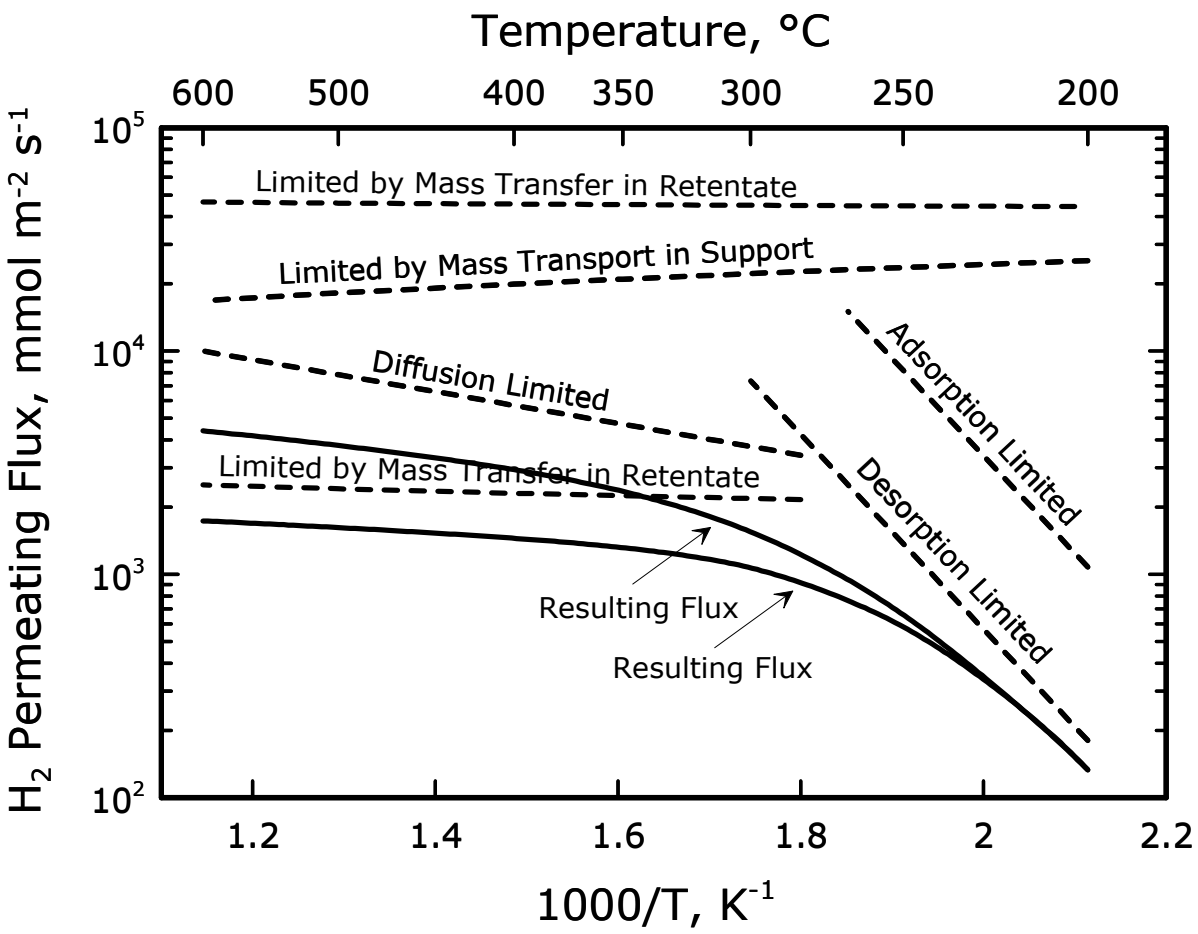
Step resistances to flux – Turbulent flow



$$R.R. \equiv \frac{\Delta P_{H_2}^{Step_j}}{\Delta P_{H_2}^{Tot}}$$

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

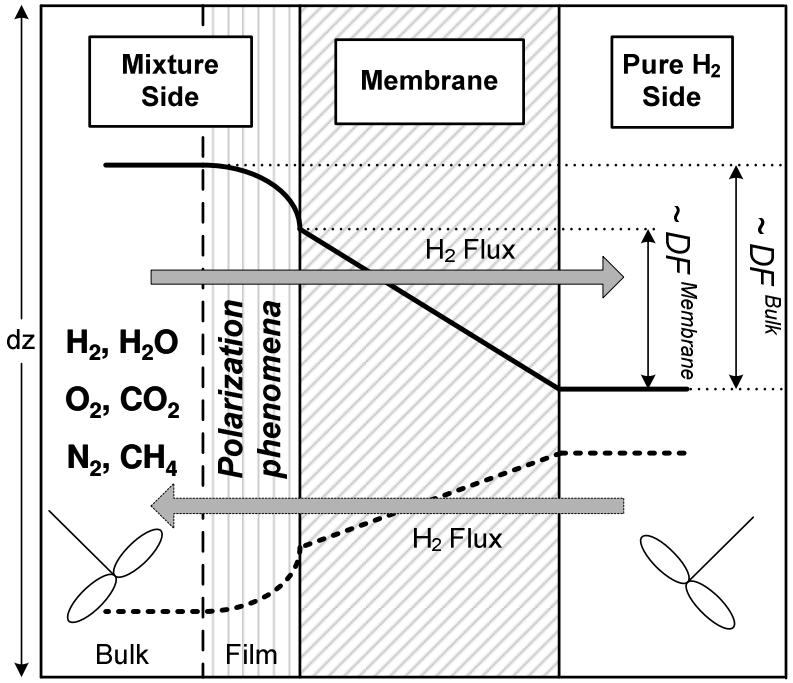
Flux vs. T – Laminar and Turbulent flow



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



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

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

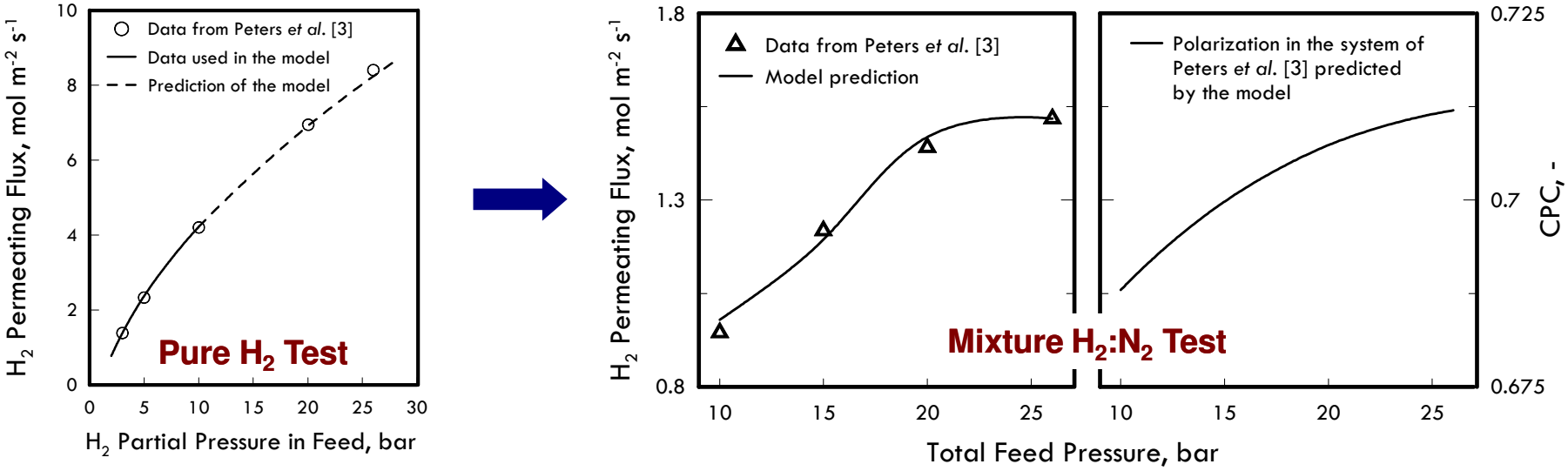
$$DF \equiv DF^{Sieverts} \equiv \Delta\sqrt{P_{H_2}} = \left(\sqrt{P_{H_2}^{Upstream}} - \sqrt{P_{H_2}^{Downstream}}\right)$$

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

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

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

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

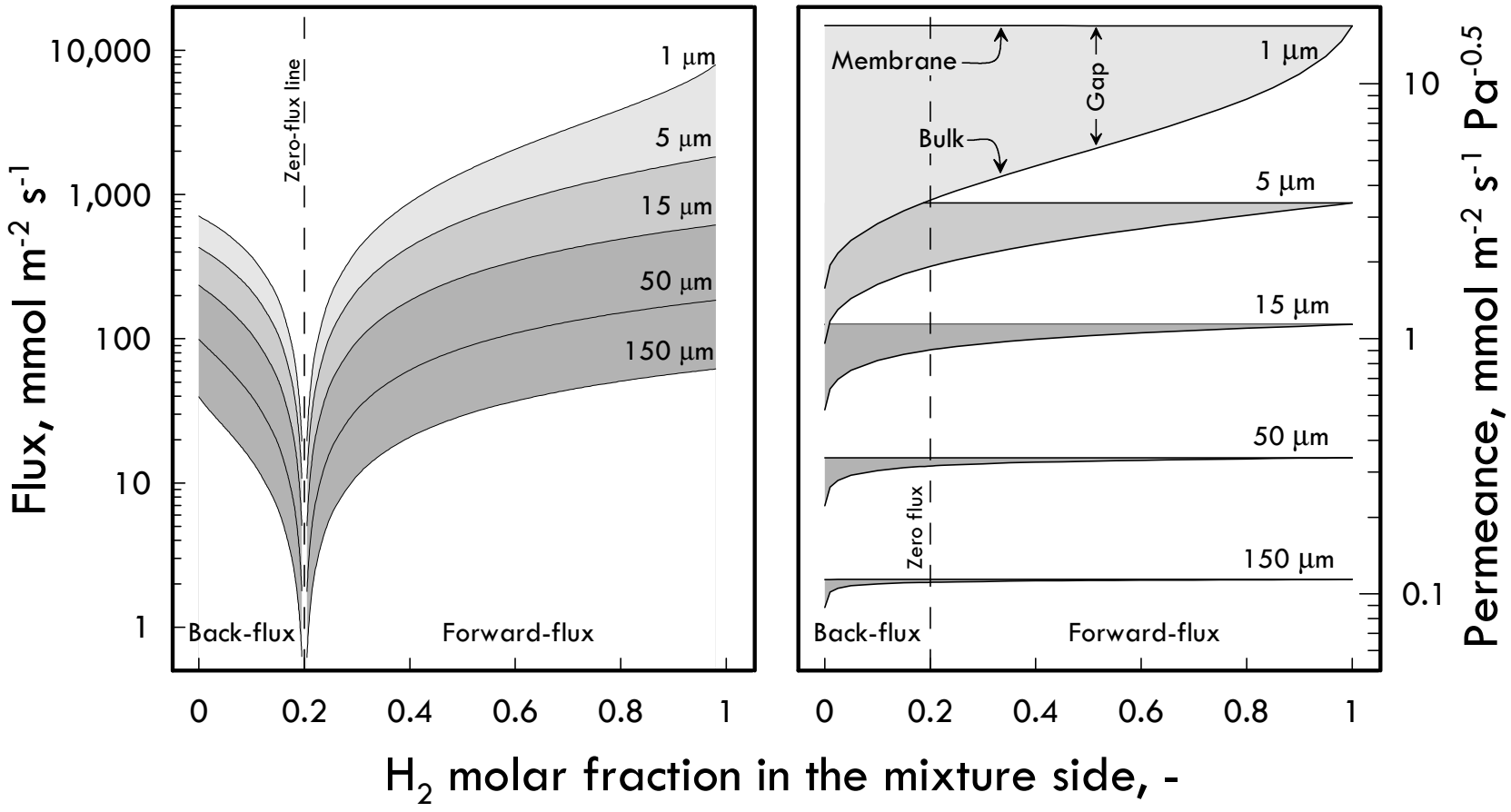
[3] Peters T.A. *et al.*, 2008. *J. Mem. Sci.*, 316: 119-127.

Polarization analysis - Operating conditions

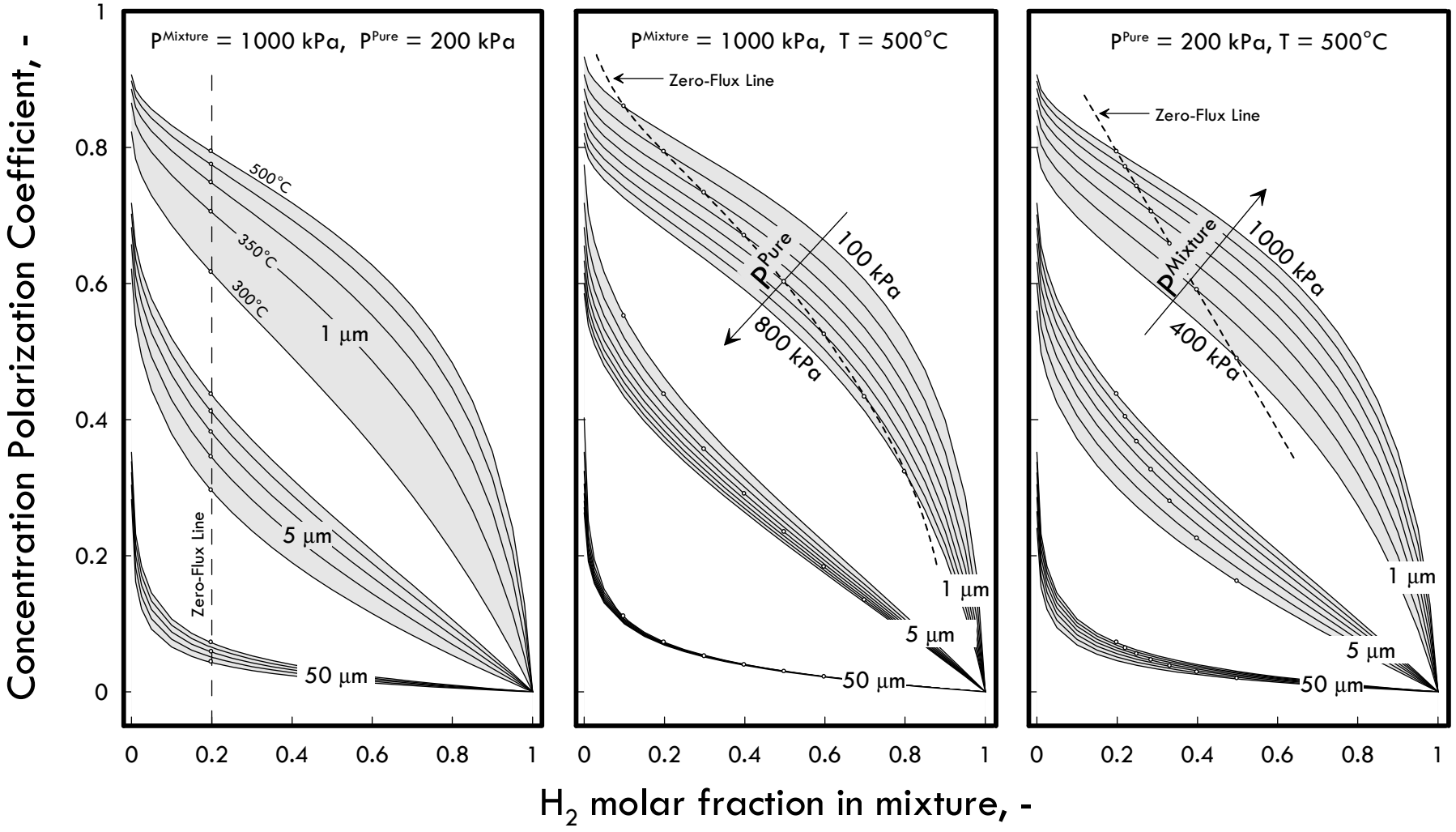
Side	Molar fraction, -						Total pressure, kPa	Reynolds number, -
	H_2	CH_4	CO_2	H_2O	O_2	N_2		
Mixture	{0 ... 1}	{0.2 ... 0} for each species					{100 ... 1000}	2100 - 8000
Pure H_2	1	Absent					{100 ... 800}	Not influent
Temperatures = [300 - 500]ºC								

Flux and permeance vs. x_{H_2}

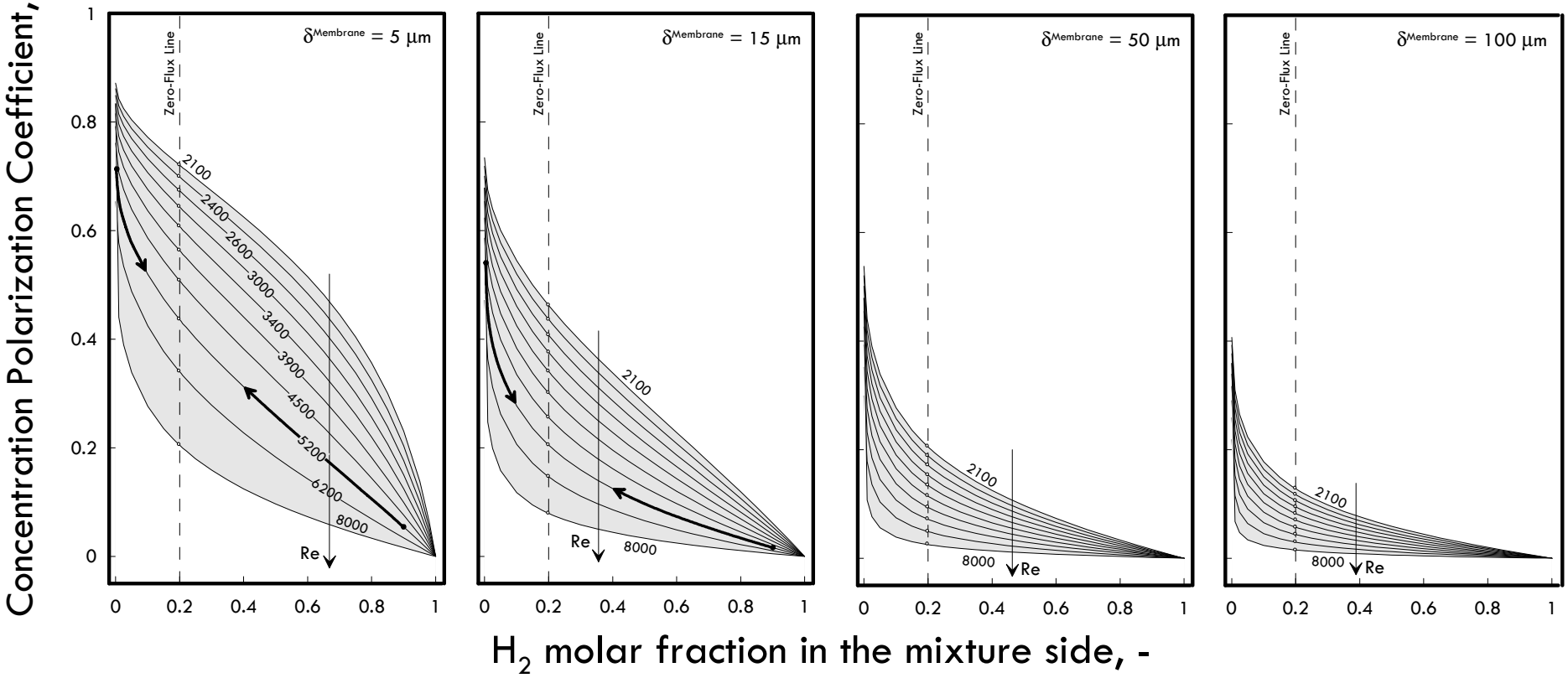
$P^{Mixture}$ = 1000 kPa, P^{Pure} = 200 kPa, T = 500 °C, Re @ 5200



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