

Membrane processes for gas separation

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Lecture 11

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Intended learning outcome

- Understand how separation via membranes works
- Describe mass transfer mechanisms inside the membrane module
- Learn how to simulate and design membrane processes

THEORY

- What is a membrane stage?
- How to calculate transmembrane flux?
- How to model a membrane stage?
- How to design multi-stage processes?
- Which non-ideal phenomena should be accounted for?

EXERCISE

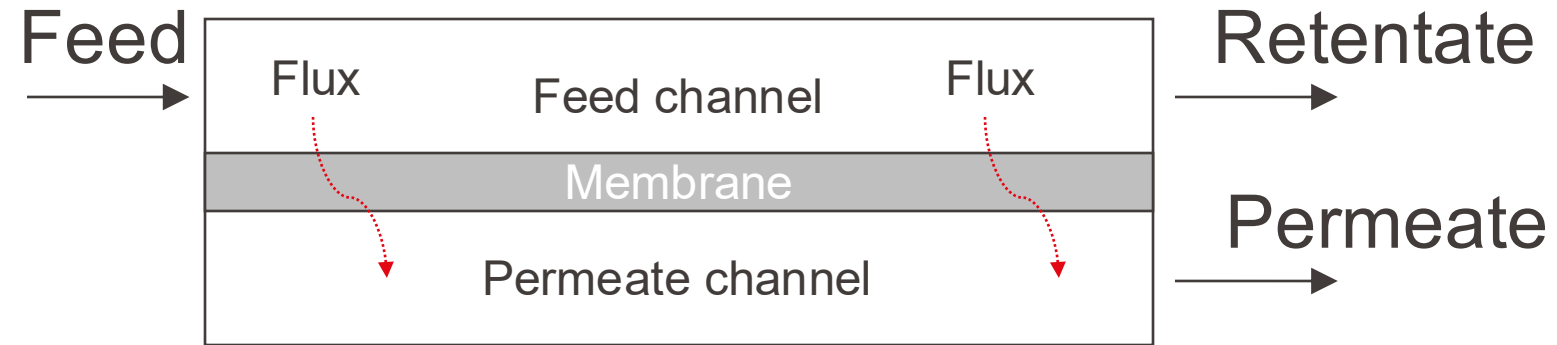
- ✓ Building the model for a single stage
- ✓ Building the model for a double stage
- ✓ Simulations

Group projects presentations on 16.12

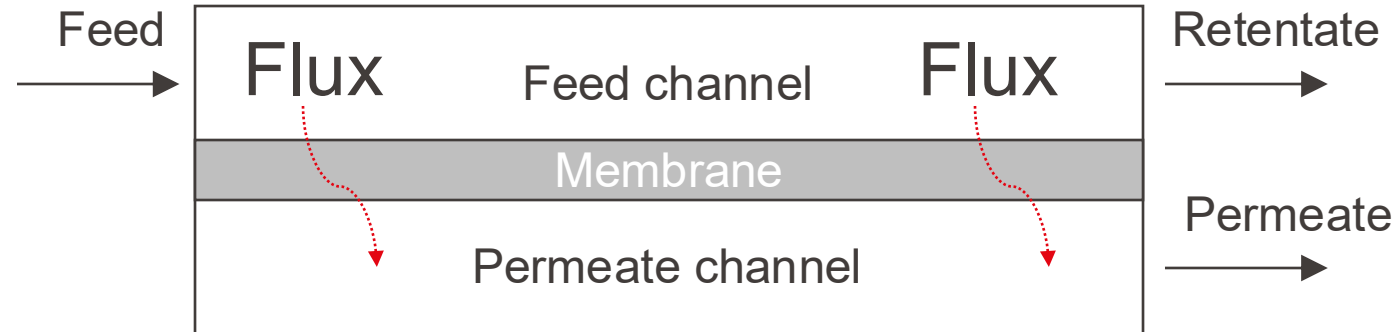
- Groups of 5 students (10 groups) → ~ 12 minutes per group (presentation + questions)

- Group work:
 - build your model for the single stage and the double stage process (without recycle)
 - Validate the model by comparing some exemplary results.
 - Assess the impact of given inputs and parameters on the outputs

Membrane module



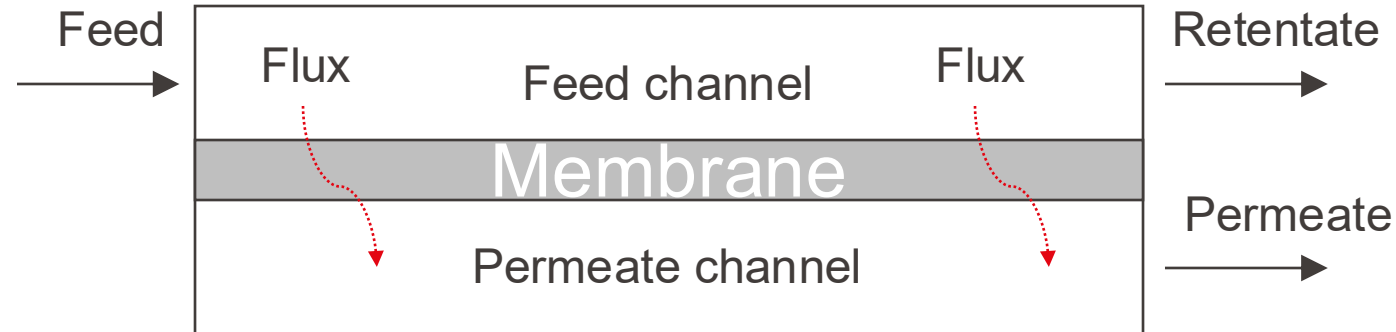
Membrane module, definitions



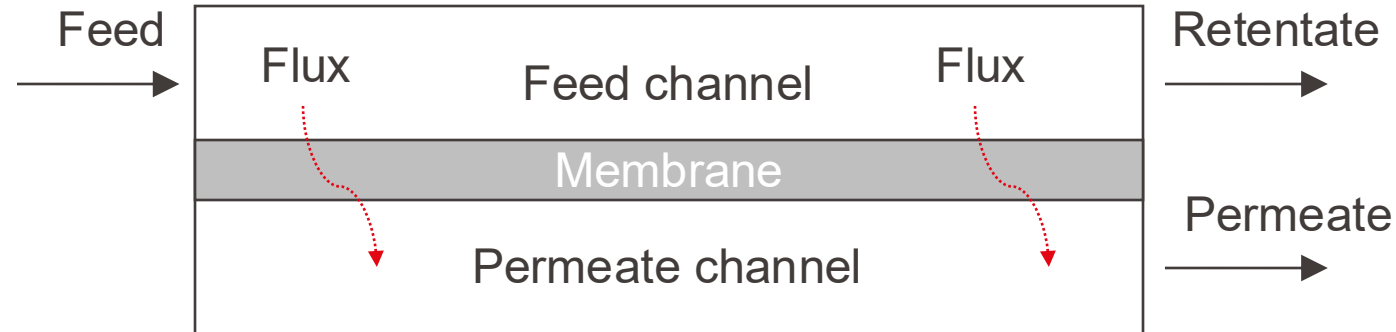
$$\text{Transmembrane flux } \left[\frac{\text{mol}}{\text{m}^2 \text{s}} \right] = k \times \text{driving force} =$$

$$= \text{Mass transfer coefficient} \times \text{chemical potential gradient}$$

Membrane module, definitions



- ✓ **Membrane permeance:** measure of the flux of a component through the membrane for a given driving force;
- ✓ **Membrane selectivity:** ratio between the permeance of two components = $\frac{\text{Permeance A}}{\text{Permeance B}}$



Outputs

- ✓ **Product recovery:** ratio between the content of the product in the permeate stream and the content in the feed stream $= \frac{Q_{i,p}}{Q_{i,f}} = \frac{X_{i,p}Q_p}{X_{i,f}Q_f}$
- ✓ **Product purity:** concentration of the product in the outlet permeate stream $= X_{i,p}$

Overall balances on the membrane stage

- Total mass balance

$$Q_f = Q_r + Q_p$$

- Mass balance for component i

$$X_{i,f} Q_f = X_{i,r} Q_r + X_{i,p} Q_p$$

$$\sum X_{i,f} = \sum X_{i,r} = \sum X_{i,p} = 1$$

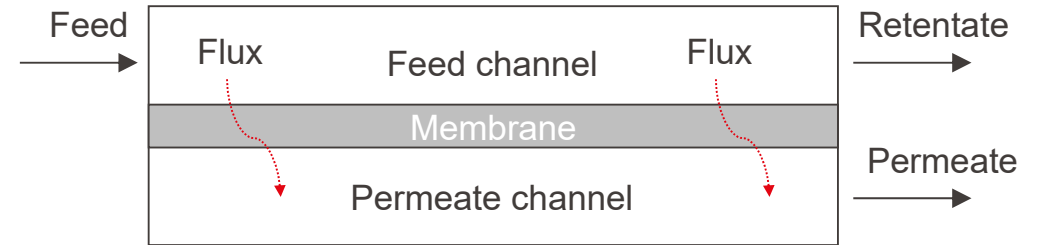
- Total mass balance on the feed channel

$$Q_f = Q_r + \int_0^A J dA$$

- Mass balance for component i on the feed channel

$$X_{i,f} Q_f = X_{i,r} Q_r + \int_0^A J_i dA$$

$$\sum J_i = J$$

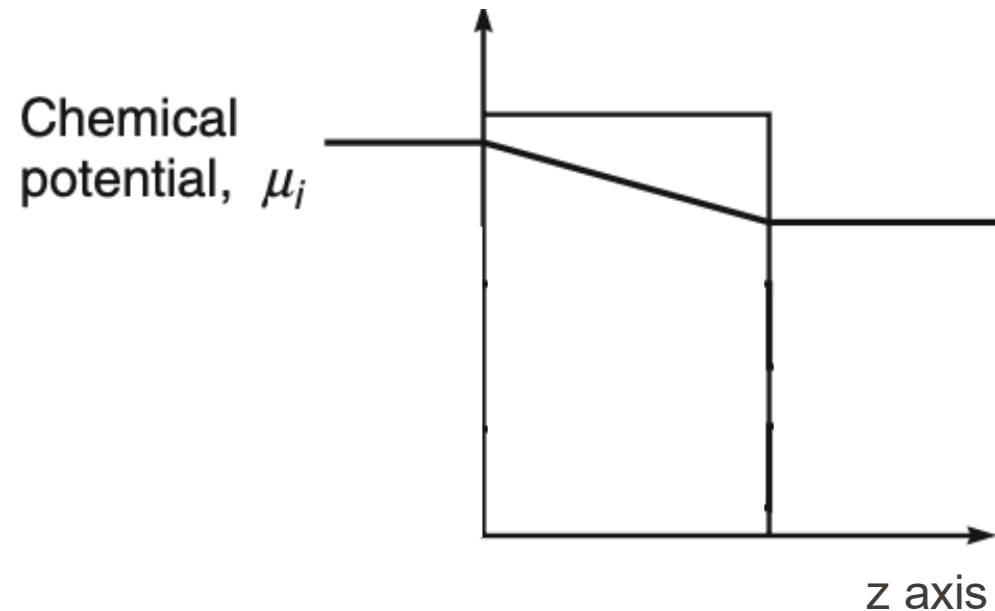


How do we
calculate J ?

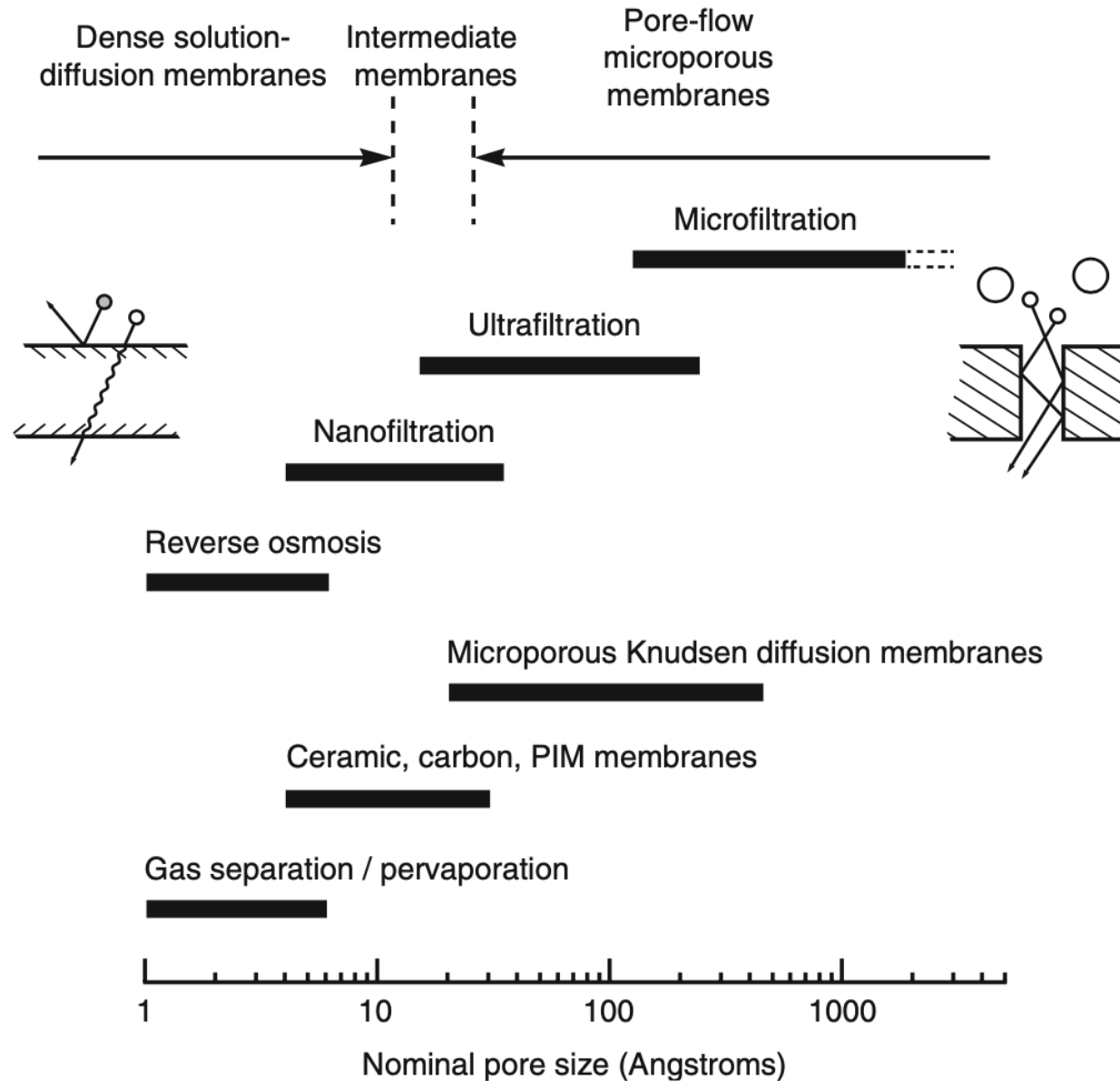
- Generic definition of the flux as function of chemical potential gradient

$$J_i = -L_i \frac{d\mu_i}{dz}$$

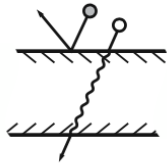
$$d\mu_i = RT \, d\ln(\gamma_i X_i) + v_i \, dp$$



Transport mechanism through the membrane



Dense membranes

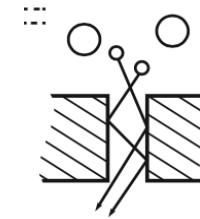


Flux driven by the **concentration gradient**

Transport based on solution-diffusion

Selectivity based on solubility and diffusivity

Porous membranes



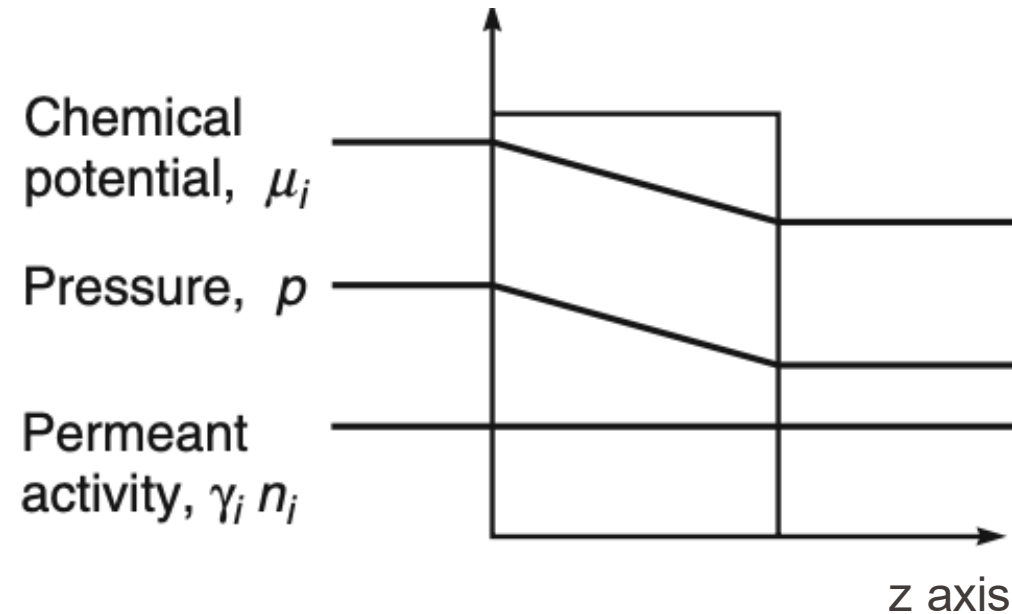
Flux driven by the total **pressure gradient**

Transport based on viscous flow and diffusion

Selectivity based on pore size

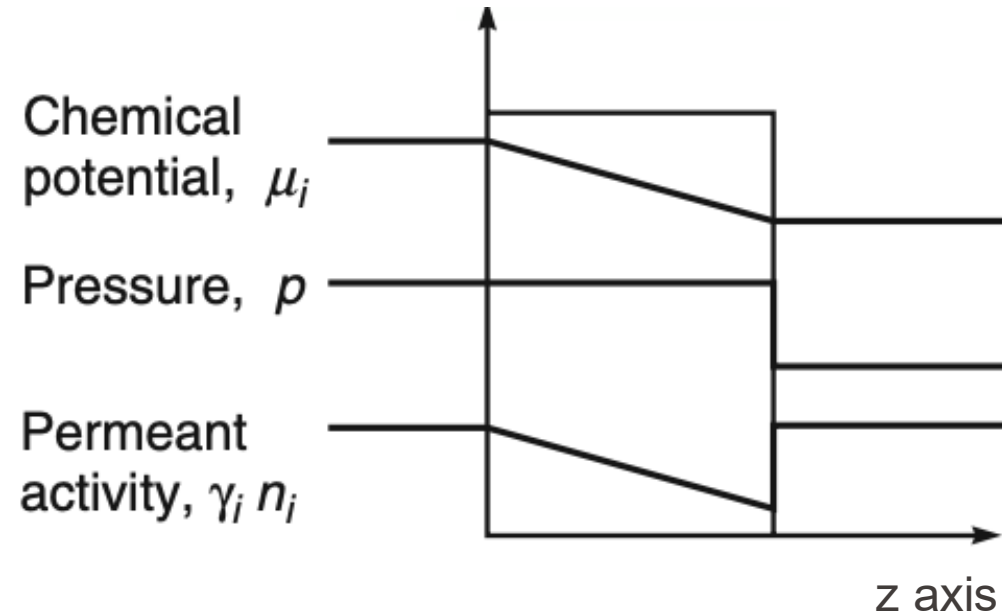
Porous membranes

- Pore-flow model assumes that concentration is uniform within the membrane -> only pressure gradient



Dense membranes

- Solution-diffusion model assumes that pressure is uniform within the membrane -> only concentration gradient



$$J_i = -L_i \frac{d\mu_i}{dz} = -L_i RT \frac{d \ln(\gamma_i X_i)}{dz} = -L_i \frac{RT}{X_i} \frac{dX_i}{dz}$$

uniform pressure

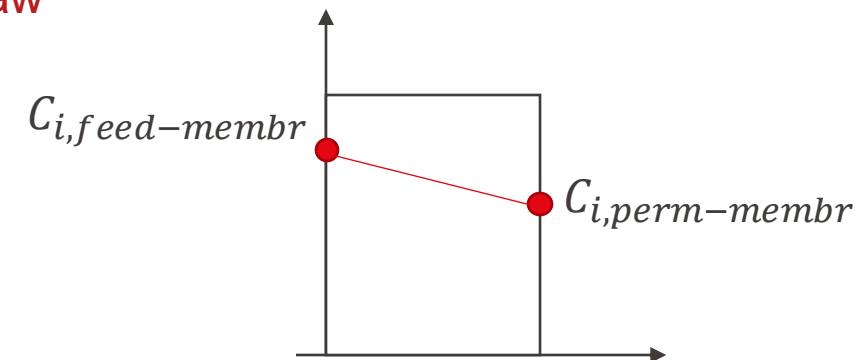
When we refer to the concentration C_i [kg/m³]

$$J_i = -L_i \frac{RT}{C_i} \frac{dC_i}{dz} = -D_i \frac{dC_i}{dz} \quad \longrightarrow \quad \frac{D_i}{\delta} (C_{i,feed-membr} - C_{i,perm-membr})$$

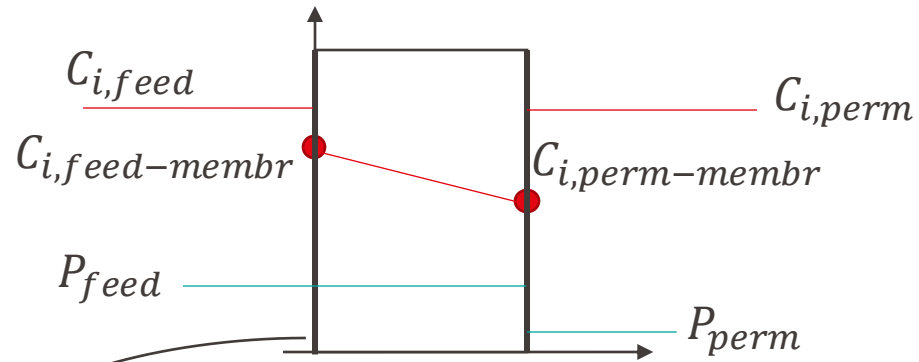
same form as the Fick's law

We need a function of the concentrations in the gaseous phase:

$$C_{i,feed} - C_{i,perm}$$



Flux from solution-diffusion model in gas separation



Equation of the chemical potentials at the gas-membrane interface

$$\mu_{i,gas} = \mu_{i,membrane}$$

compressible incompressible

Feed-membrane interface

$$\mu_i^0 + RT \ln(\gamma_i^G X_{i,feed}) + RT \ln\left(\frac{p_{feed}}{p_{i,sat}}\right) = \mu_i^0 + RT \ln(\gamma_i^{membr} X_{i,feed-membr}) + v_i(p_{feed} - p_{i,sat})$$

$$X_{i,feed-membr} = \frac{\gamma_i^G X_{i,feed} \frac{p_{feed}}{p_{i,sat}}}{\gamma_i^{membr}} \exp\left(-\frac{v_i(p_{feed} - p_{i,sat})}{RT}\right)$$

$$C_{i,feed-membr} = \frac{\gamma_i^G m_i \rho_m \frac{p_{i,feed}}{p_{i,sat}}}{\gamma_i^{membr}} \exp\left(-\frac{v_i(p_{feed} - p_{i,sat})}{RT}\right)$$

$K_{i,G}$

Feed-membrane interface

$$C_{i,feed-membr} = K_{i,G} p_{i,feed} \exp\left(-\frac{v_i(p_{feed} - p_{i,sat})}{RT}\right)$$

Permeate-membrane interface

$$C_{i,perm-membr} = K_{i,G} p_{i,perm} \exp\left(-\frac{v_i(p_{feed} - p_{i,sat})}{RT}\right)$$

v_i molar volume in the membrane material

$$J_i = -D_i \frac{dC_i}{dz} = \frac{D_i K_{i,G} (p_{i,feed} - p_{i,perm})}{l} \times \exp\left(-\frac{v_i(p_{feed} - p_{i,sat})}{RT}\right) \quad \text{Poynting correction } \sim 1$$

Partial pressure difference
across the membrane

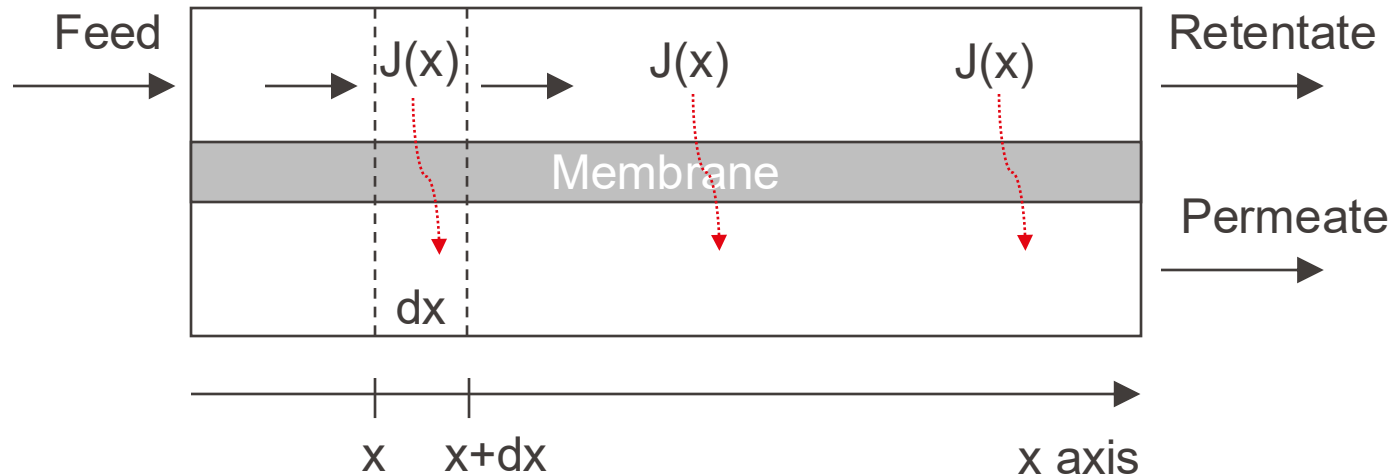
Total pressure on the feed side

$$J_i = \frac{D_i K_{i,G} (p_{i,feed} - p_{i,perm})}{l} = \frac{P_{i,G} (p_{i,feed} - p_{i,perm})}{l}$$

Permeability coefficient $P_{i,G}$ given by the product of diffusivity D_i and sorption coefficient $K_{i,G}$

1-dimensional model: discretization along the direction of the feed stream (x axis)

Co-current flow arrangement



Assumptions

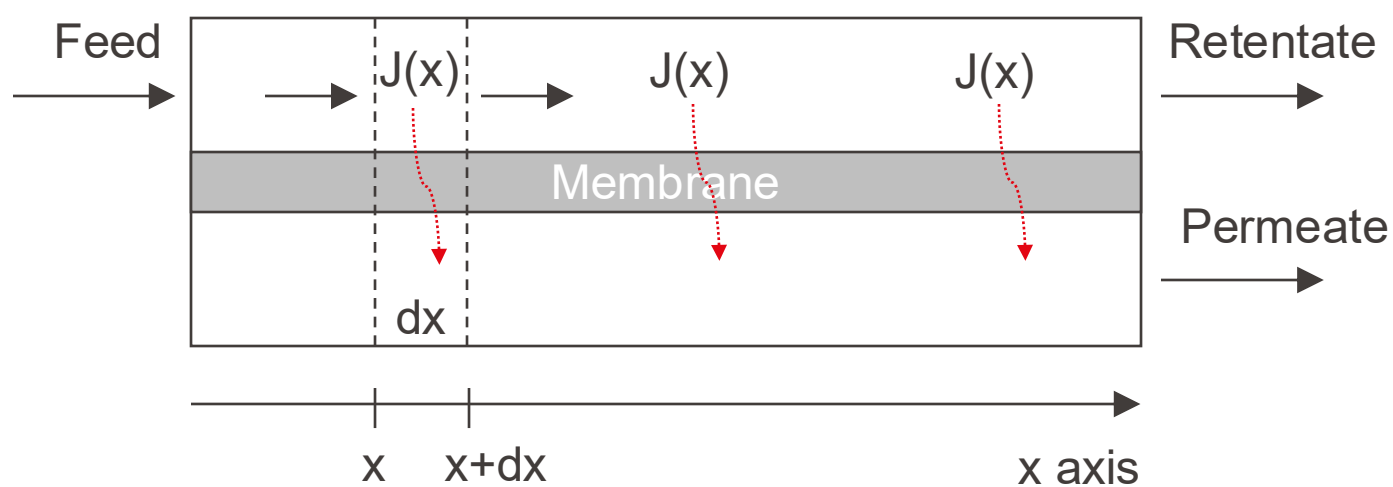
- No variation along the width
- Permeance independent of X
- Negligible pressure drops
- Isothermal process
- Well mixed feed and permeate channels

$$J_i(x) = \frac{P_{i,G} (p_{i,feed}(x) - p_{i,perm}(x))}{l} = P_i (P_{feed} X_{i,feed}(x) - P_{perm} X_{i,perm}(x))$$

$$J(x) = \sum_{components} J_i(x)$$

1-dimensional model: discretization along the direction of the feed stream (x-axis)

Co-current flow arrangement



$$J_i(x) = \frac{P_{i,G} (p_{i,feed}(x) - p_{i,perm}(x))}{l}$$

$$= P_i (P_{feed} X_{i,feed}(x) - P_{perm} X_{i,perm}(x))$$

$$J(x) = \sum_{components} J_i(x)$$

Feed side

$$Q_r(x) = Q_f(x) - J(x) dA$$

$$X_{i,r}(x) Q_r(x) = X_{i,f}(x) Q_f(x) - J_i(x) dA$$

$$Q_f(x + 1) = Q_r(x)$$

$$X_f(x + 1) = X_r(x)$$

Permeate side

$$Q_p(x) = Q_{feed} - Q_r(x)$$

$$X_{i,p}(x) Q_p(x) = X_{i,feed} Q_{feed} - X_{i,r}(x) Q_r(x)$$

Modelling a membrane module

Equation	N equation
$J_i(x) = P_i (P_{feed} X_{i,feed}(x) - P_{perm} X_{i,perm}(x))$	$N_{components} \times N_{elem}$
$J(x) = \sum_{components} J_i(x)$	N_{elem}
$Q_r(x) = Q_f(x) - J(x) dA$	N_{elem}
$X_{i,r}(x) Q_r(x) = X_{i,f}(x) Q_f(x) - J_i(x) dA$	$N_{components} \times N_{elem}$
$Q_p(x) = Q_{feed} - Q_r(x)$	N_{elem}
$X_{i,p}(x) Q_p(x) = X_{i,feed} Q_{feed} - X_{i,r}(x) Q_r(x)$	$N_{components} \times N_{elem}$
$Q_f(x+1) = Q_r(x)$	$N_{elem} - 1$
$X_{i,f}(x+1) = X_{i,r}(x)$	$N_{components} \times (N_{elem} - 1)$
$Q_f(0) = Q_{feed}$	1
$X_{i,f}(0) = X_{i,feed}$	$N_{components}$
	total: $4 N_{components} \times N_{elem} + 4 N_{elem}$

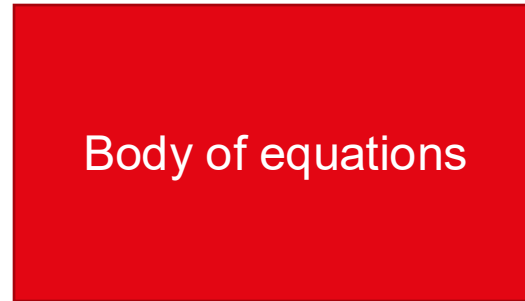
Variable	N variable
$J_i(x)$	$N_{components} \times N_{elem}$
$J(x)$	N_{elem}
$Q_r(x)$	N_{elem}
$X_{i,r}(x)$	$N_{components} \times N_{elem}$
$Q_p(x)$	N_{elem}
$X_{i,p}(x)$	$N_{components} \times N_{elem}$
$Q_f(x)$	N_{elem}
$X_{i,f}(x)$	$N_{components} \times N_{elem}$
	total: $4 N_{components} \times N_{elem} + 4 N_{elem}$

For given P_{feed} , P_{perm} and A

$$N_{equations} = N_{variables}$$

Simulation

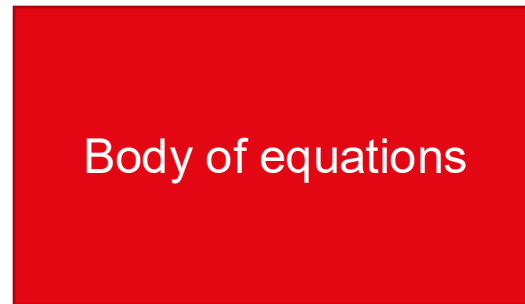
Design variable (**A**) and
operating conditions
(\mathbf{P}_{feed} , \mathbf{P}_{perm})



Recovery and purity

Design

Recovery and
purity targets

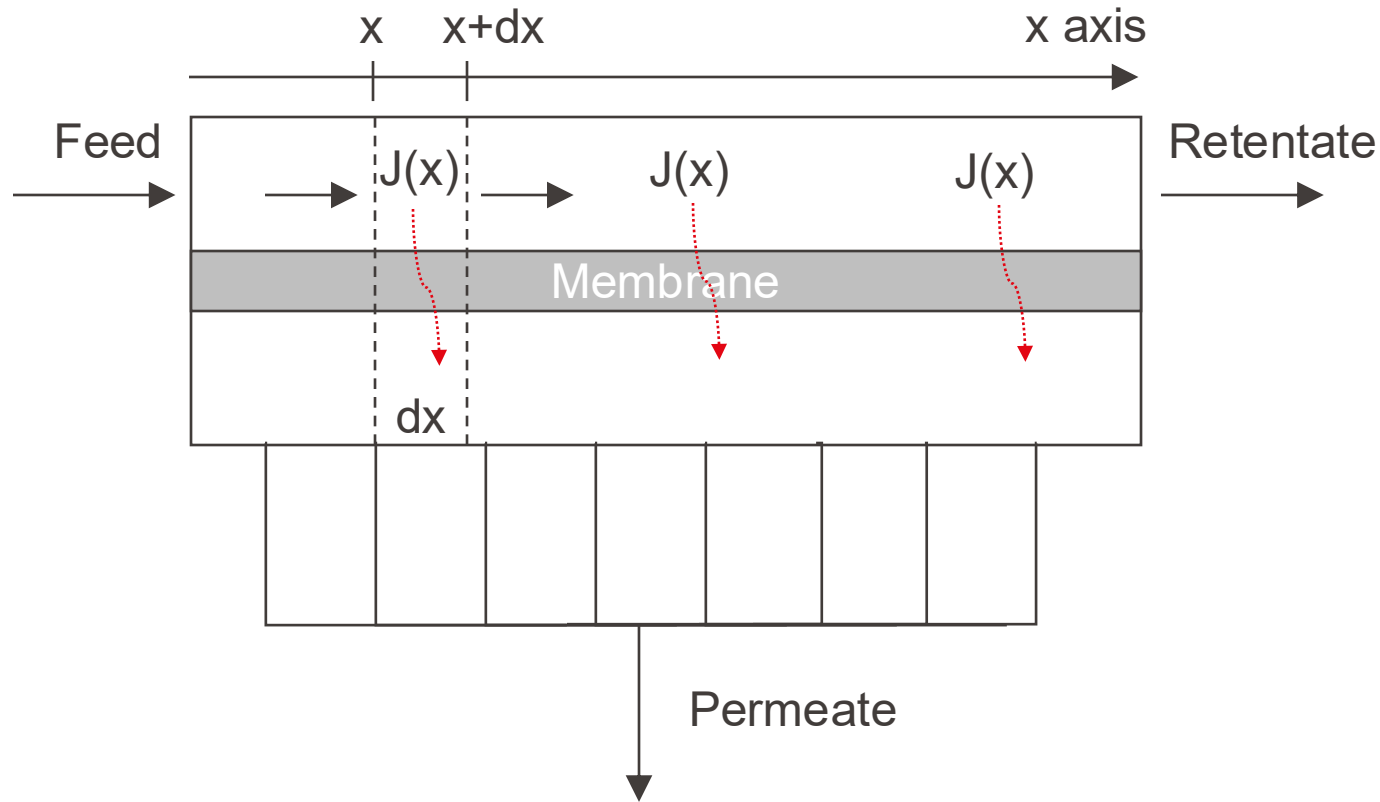


Design variable (**A**) and \mathbf{P}_{perm}



\mathbf{P}_{feed}

Cross-current flow arrangement



No mixing in the permeate channel

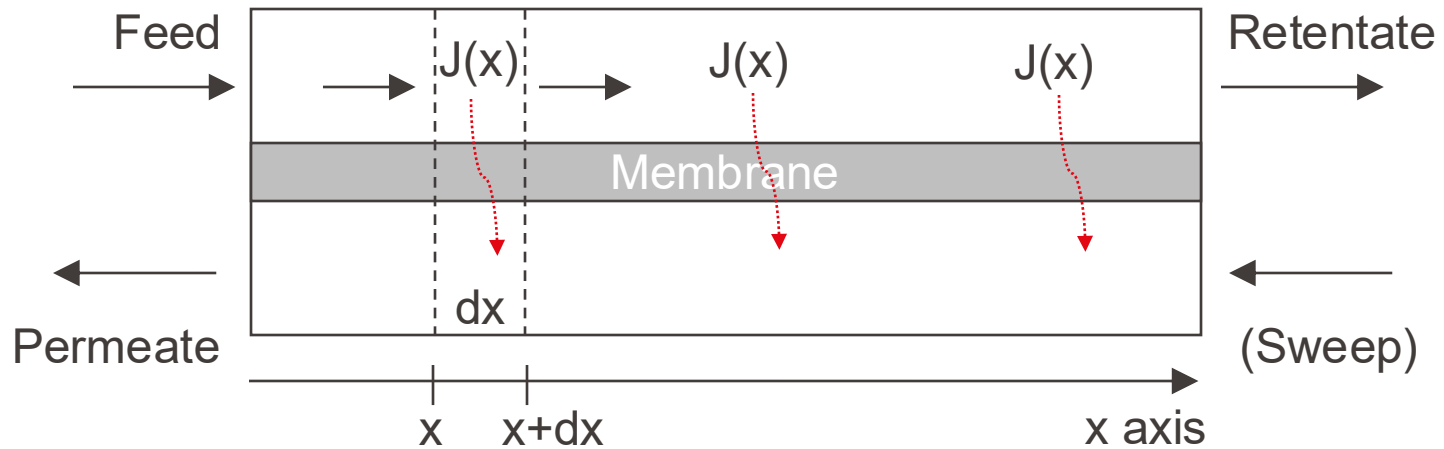
$$J_i(x) = \frac{P_{i,G} (p_{i,feed}(x) - p_{i,perm}(x))}{l}$$

$$= \mathbf{P}_i (P_{feed} X_{i,feed}(x) - P_{perm} \mathbf{X}'_{i,perm}(x))$$

$$Q_{p,out} = \sum_{x=0}^L J(x) dA$$

$$X_{i,p,out} = \frac{\sum_{x=0}^L J_i(x) dA}{Q_{p,out}}$$

Counter-current flow arrangement



$$J_i(x) = \frac{P_{i,G} (p_{i,feed}(x) - p_{i,perm}(x))}{l}$$

$$= P_i (P_{feed} X_{i,feed}(x) - P_{perm} X_{i,perm}(x))$$

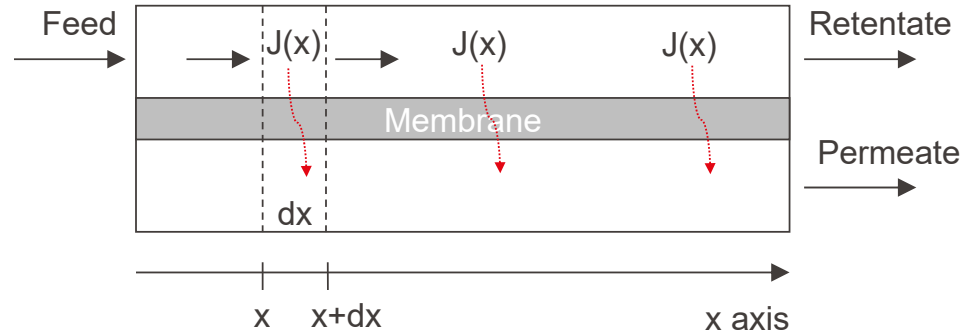
Permeate side

$$Q_p(x) = Q_p(x + dx) + J(x) dA$$

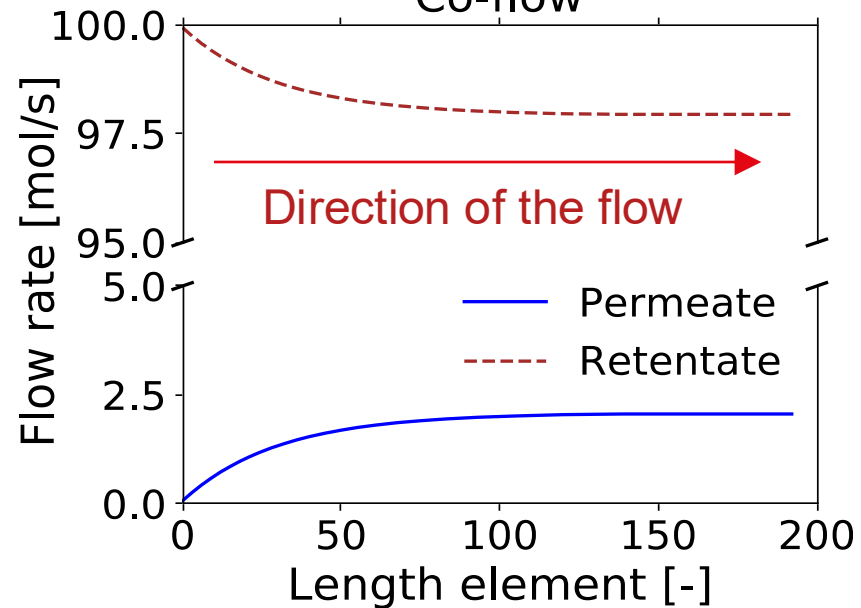
$$X_{i,p}(x) Q_p(x) = X_{i,p}(x + dx) Q_p(x + dx) + J_i(x) dA$$

Profiles along the membrane module

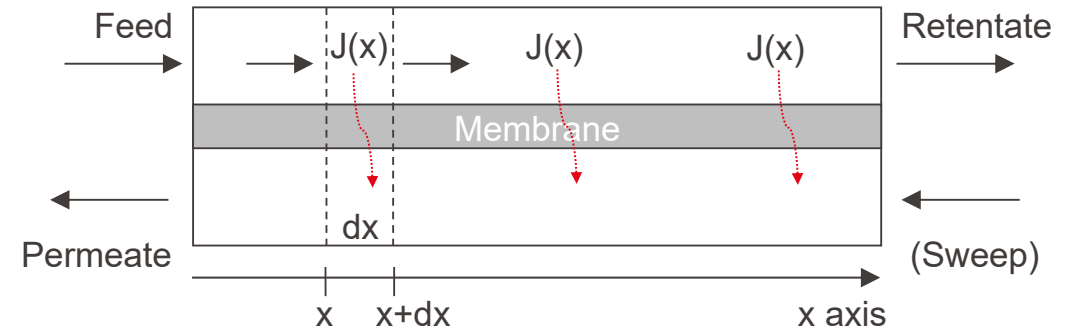
Co-current flow arrangement



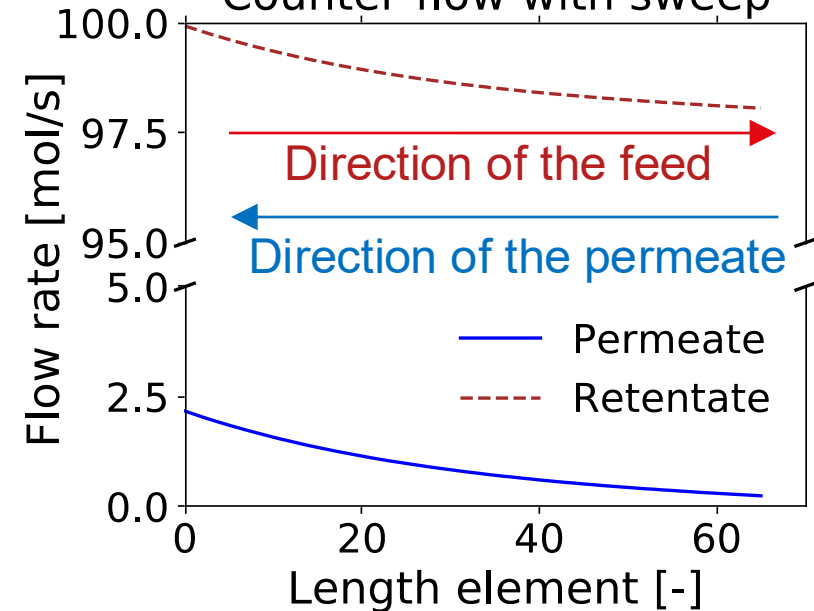
Co-flow



Counter-current flow arrangement



Counter-flow with sweep



■ Reduced driving force along the length

■ Almost constant driving force along the length

To achieve purity and recovery > 90% with one module, one would need very high permeance and selectivity & very high driving force (high P_{feed} , low P_{perm})

$$J_i(x) = P_i \left(P_{feed} X_{i,feed}(x) - P_{perm} X_{i,perm}(x) \right) > 0 \text{ if } \frac{P_{feed}}{P_{perm}} > \frac{X_{i,perm}}{X_{i,feed}} \quad \text{Max separation limited by pressure ratio}$$

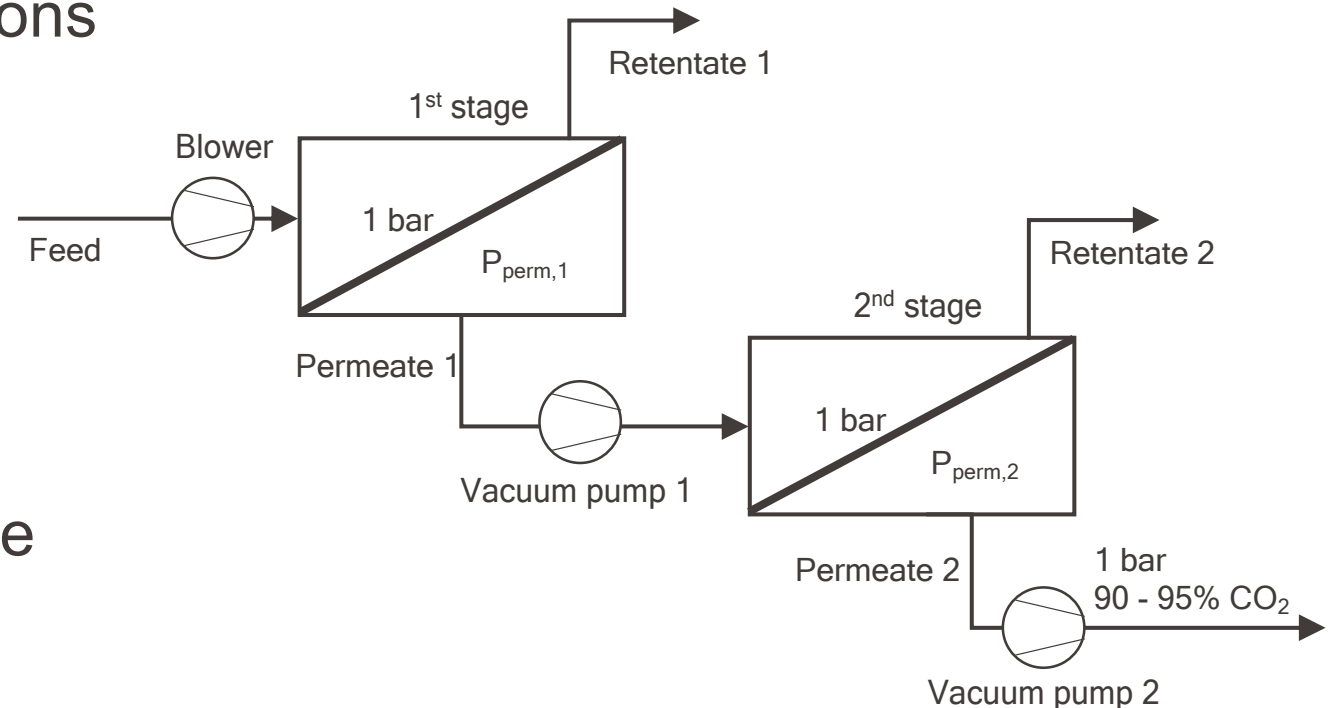
Alternative: multi-stage configurations

$$Q_{feed,2} = Q_{perm,1}$$

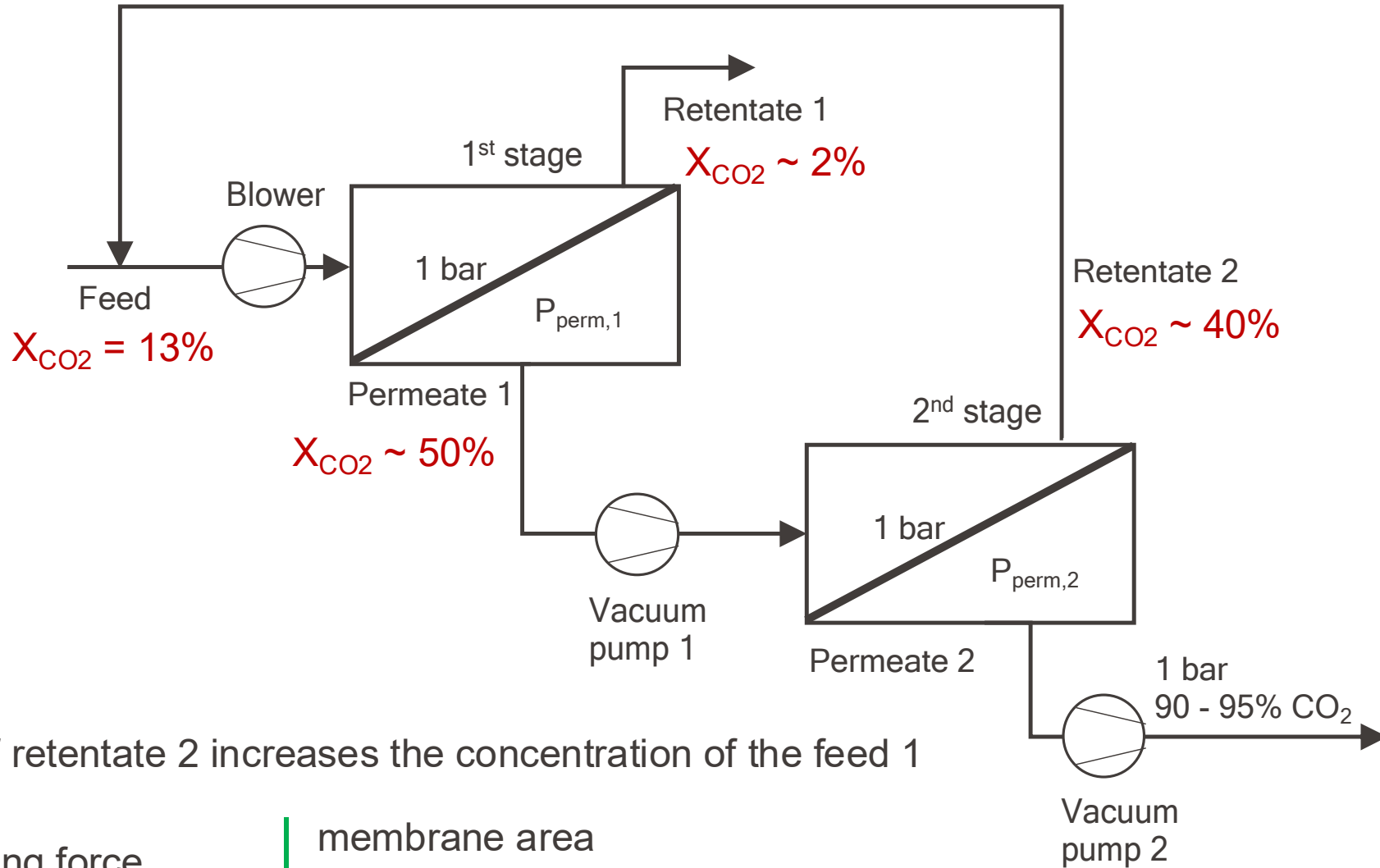
$$X_{CO_2,feed,2} = X_{CO_2,perm,1}$$



Higher driving force in the 2nd stage



Recycle design

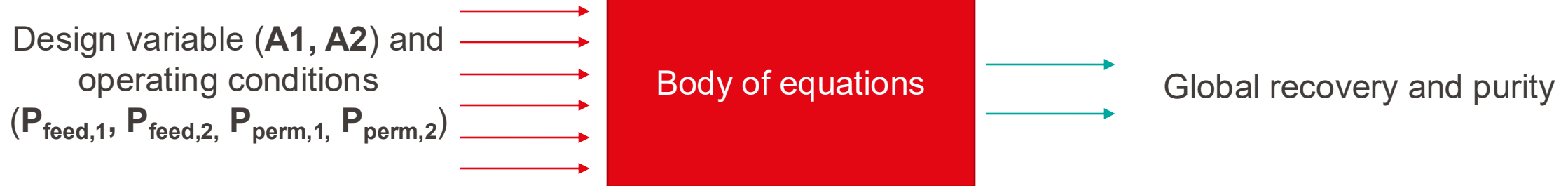


Recycle of retentate 2 increases the concentration of the feed 1

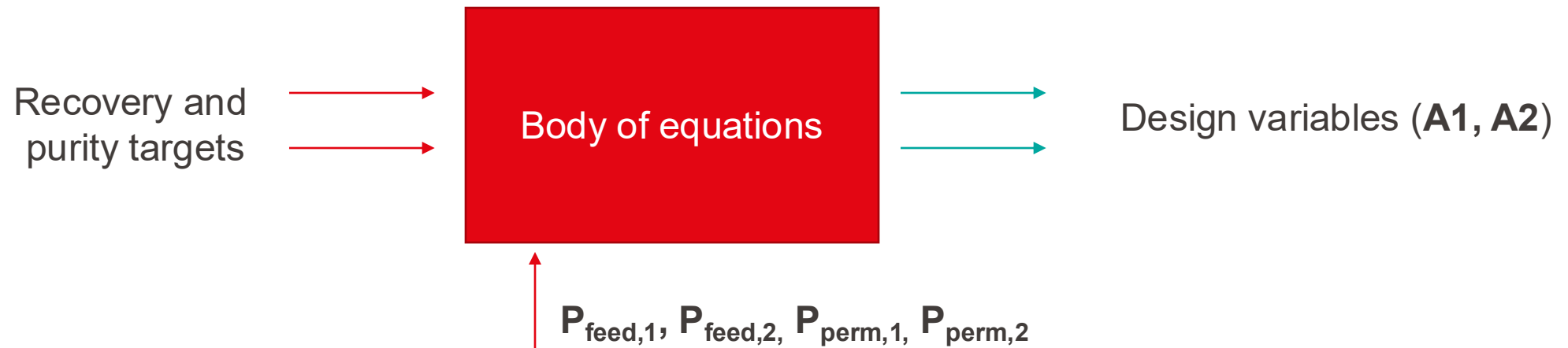
↑ driving force

↓ membrane area
energy

Simulation



Design



THEORY

- What is a membrane stage?
- How to calculate transmembrane flux?
- How to model a membrane stage?
- How to design multi-stage processes?
- Which non-ideal phenomena should be accounted for?

EXERCISE

- ✓ Building the model to simulate a single stage
- ✓ Building the model to simulate a double stage (without recycle)
- ✓ Simulations

Building the model to simulate a single-stage

Inputs:

- feed concentration (CO_2, N_2)
- feed flow rate [mol/s]
- feed pressure [bar]
- permeate pressure [bar]
- membrane area [m^2]

Parameters:

- membrane permeance
[GPU to convert in $\text{mol}/(\text{m}^2\text{sPa})$]
- membrane CO_2/N_2 selectivity
- geometrical properties
(width B: 1 m,
discretization element dx: 0.1 m)

class single stage

Outputs:

- permeate concentration
- permeate flow rate
- retentate concentration
- retentate flow rate
- recovery
- purity

method solver:

- flux definition
- total flux definition
- mass balance on the retentate
- mass balance on the permeate
- next element feed definition

Model for the single-stage process

Solver

Binary mixture (CO₂-N₂)

Negligible pressure drops and concentration polarization

Cross-current flow arrangement

for i in range (N_elem):

$$X'_{CO_2,p}[i] = \frac{1+(\alpha-1)(\beta+X_{CO_2,f}[i]) - \sqrt{[1+(\alpha-1)(\beta+X_{CO_2,f}[i])]^2 - 4\alpha\beta(\alpha-1)X_{CO_2,f}[i]}}{2\beta(\alpha-1)}$$

$$J_{CO_2}[i] = P_{CO_2} (P_{feed} X_{CO_2,f}[i] - P_{perm} X'_{CO_2,p}[i])$$

$$J_{N_2}[i] = P_{N_2} (P_{feed} X_{N_2,f}[i] - P_{perm} (1 - X'_{CO_2,p}[i]))$$

$$Q_r[i] = Q_f[i] - (J_{CO_2}[i] + J_{N_2}[i]) dA$$

$$X_{CO_2,r}[i] Q_r[i] = X_{CO_2,f}[i] Q_f[i] - (J_{CO_2}[i]) dA$$

$$\left. \begin{aligned} Q_f[i+1] &= Q_r[i] \\ X_f[i+1] &= X_r[i] \end{aligned} \right\} \text{if } i \neq N_elem - 1$$

Output: $Q_{ret,out} = Q_r[-1]$

$$X_{CO_2,ret\ out} = X_{CO_2,r}[-1]$$

$$Recovery = \frac{Q_{perm,out} X_{CO_2,perm\ out}}{X_{f,CO_2}[0] Q_f[0]}$$

■ $Q_{perm,out} = Q_f[0] - Q_{ret,out}$

$$X_{CO_2,perm\ out} = Purity = \frac{X_{f,CO_2}[0] Q_f[0] - X_{CO_2,ret\ out} Q_{ret,out}}{Q_{perm,out}}$$

α selectivity

β pressure ratio: $\frac{P_{perm}}{P_{feed}}$

Building the model to simulate a double-stage

Inputs:

- feed concentration
- feed flow rate
- feed pressure (1 and 2)
- permeate pressure (1 and 2)
- membrane area (1 and 2)

Parameters:

- membrane permeance
- membrane selectivity
- geometrical properties



class double stage

Outputs:

- permeate concentration (1 and 2)
- permeate flow rate (1 and 2)
- retentate concentration (1 and 2)
- retentate flow rate (1 and 2)
- global recovery
- global purity

method solver:

- def stage 1 as *class* single stage (inputs stage 1, parameters stage 1)
- def feed stage 2 = permeate stage 1
- def stage 2 as *class* single stage (inputs stage 2, parameters stage 2)

Validity range Single stage

Permeance = 10000 GPU, $S_{el} = 30$

Standard set: $P_f = 1$ bar, $P_p = 0.1$ bar, $X_f = 0.1$, $Q_f = 2.5$ mol/s, $A = 10$ m²

-> recovery = 0.41, purity = 0.51 [exemplary result for validation]

- A membrane: 1 -100 m²
- P permeate: 0.01 – 0.5 bar
- Pfeed: 1 – 5 bar
- Qfeed: 1 – 100 mol/s
- X_f : 0.01 – 0.5
- Permeance: 1000 – 10000 GPU
- Selectivity: 20-100

Validity range Double stage

Permeance = 10000 GPU, $S_{el} = 30$

Standard set: $P_{f1} = 1$ bar, $P_{p1} = 0.1$ bar, $P_{f2} = 1$ bar, $P_{p2} = 0.2$ bar,

$X_f = 0.1$, $Q_f = 2.5$ mol/s, $A_1 = 10$ m², $A_2 = 5$ m²

-> recovery = 0.4, purity = 0.71 [exemplary result for validation]

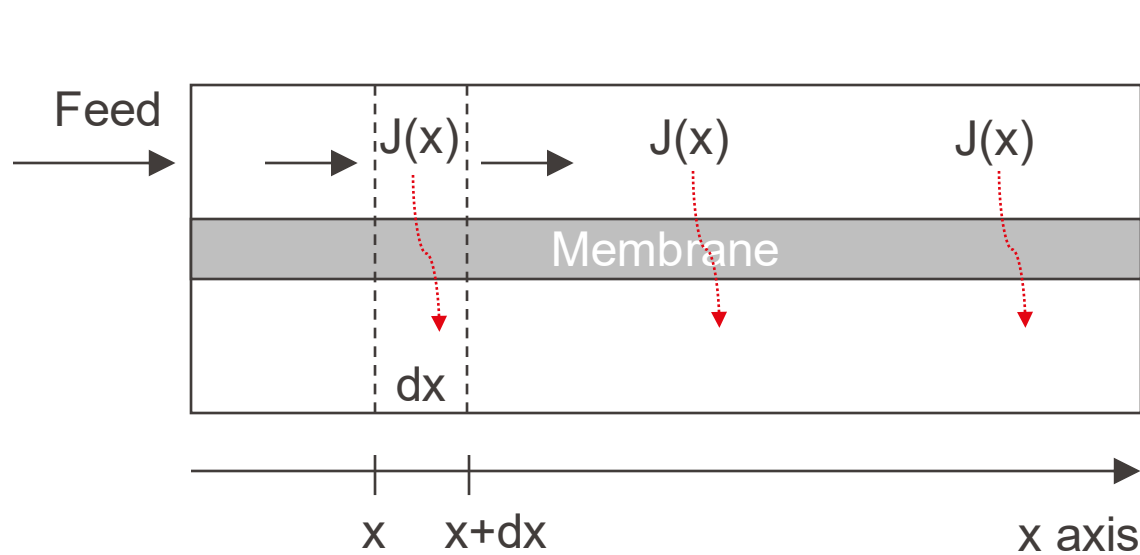
- A membrane 1: 5 - 50 m², A membrane 2: 1 - 10 m²
- P permeate 1, P permeate 2: 0.01 – 0.5 bar
- P feed 1, P feed 2: 1–5 bar
- Q feed: 1 – 100 mol/s
- X_f : 0.01 – 0.5
- Permeance: 1000 – 10000 GPU
- Selectivity: 20-100

- Group 1: influence of **feed flow rate** on single and double stage
- Group 2: influence of **feed concentration** on single and double stage
- Group 3: influence of **feed pressure** on single stage and **feed pressure 1** on double stage
- Group 4: influence of **feed pressure** on single stage and **feed pressure 2** on double stage
- Group 5: influence of **permeate pressure** on single stage and **permeate pressure 1** on double stage
- Group 6: influence of **permeate pressure** on single stage and **permeate pressure 2** on double stage
- Group 7: influence of **membrane area** on single stage and **membrane area 1** on double stage
- Group 8: influence of **membrane area** on single stage and **membrane area 2** on double stage
- Group 9: influence of **permeance** on single and double stage (same permeance for both stages)
- Group 10: influence of **selectivity** on single and double stage (same selectivity for both stages)

Group projects presentations on 16.12

Expected results for **the single and the double stage** process:

- global recovery and purity variation with the given parameter (e.g., permeance)
- profiles of CO₂ concentration in the feed and permeate channel with 2-3 values of the given parameter in the investigated range
- profiles of CO₂ and N₂ flux with 2-3 values of the given parameter in the investigated range
- profiles of flow rate in the feed channel with 2-3 values of the given parameter in the investigated range



Pressure drops \rightarrow decrease of P_{feed} along the x axis

Concentration polarization \rightarrow decrease of $X_{i,\text{feed}}$ along the y axis

$$J_i(x) = \frac{P_{i,G} (p_{i,\text{feed}}(x) - p_{i,\text{perm}}(x))}{l} = P_i (P_{\text{feed}} X_{i,\text{feed}}(x) - P_{\text{perm}} X_{i,\text{perm}}(x))$$

Non-ideal phenomena

Pressure drops in the feed channel

Pressure drops depend on the velocity v and on the friction factor f

$$\frac{dP_{feed}}{dx} = -f \frac{\rho}{2 d_{hydr}} v^2$$

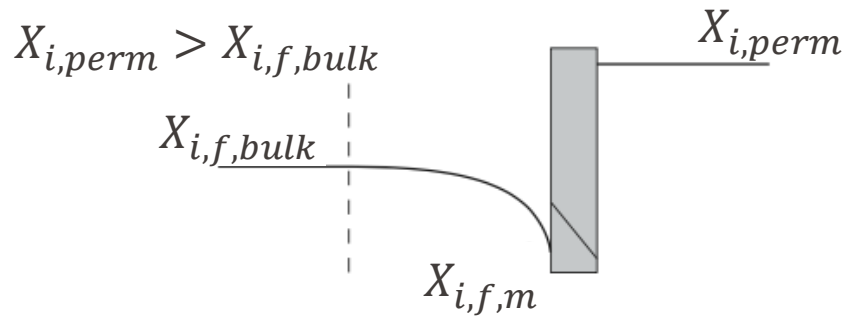
$$f = \frac{64}{Re} \quad \text{friction factor for laminar flow (Re < 2300)}$$

Common limit on pressure drops for channel design: 1.5 psi/m (0.1 bar/m)

Non-ideal phenomena

Concentration polarization

More permeable component



$$J_{i,bulk \rightarrow interface} = J_{i,transmembrane}$$

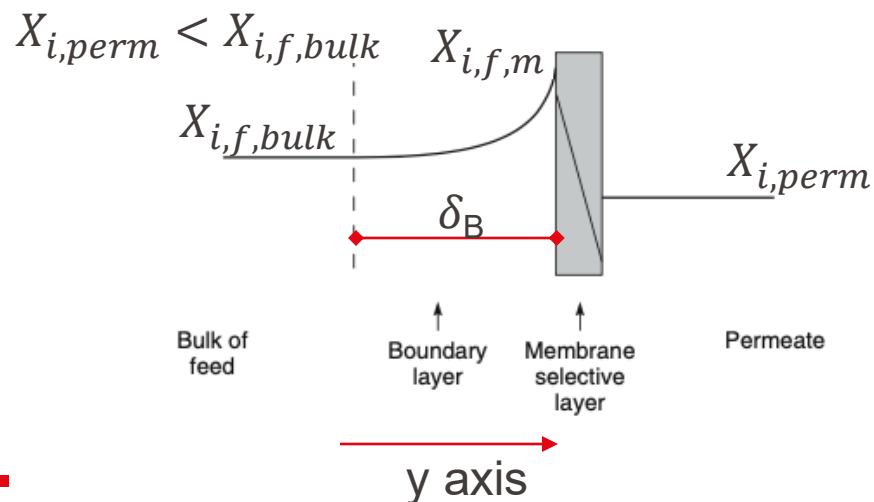
For a binary mixture and cross-current flow arrangement:

$$J_1 = P_1 (P_{feed} X_{1,f,m} - P_{perm} X'_{1,perm})$$

$$J_2 = P_2 (P_{feed} (1 - X_{1,f,m}) - P_{perm} (1 - X'_{1,perm}))$$

mass transfer coefficient k
 $k \left[\frac{mol}{m^2 s} \right] = \frac{D}{\delta_B} \frac{P}{RT}$

Less permeable component



$$J_1 = X'_{1,perm} (J_1 + J_2) = \underbrace{-D \frac{P_{feed}}{RT_{feed}} \frac{dX_{i,f}}{dy}}_{J_{i,bulk \rightarrow interface} \text{ diffusive}} + \underbrace{X_{i,f} (J_1 + J_2)}_{J_{i,bulk \rightarrow interface} \text{ convective}}$$

$$\frac{X'_{1,perm} - X_{1,f,m}}{X'_{1,perm} - X_{1,f,bulk}} = \exp\left(\frac{J_1 + J_2}{k}\right)$$

Concentration polarization

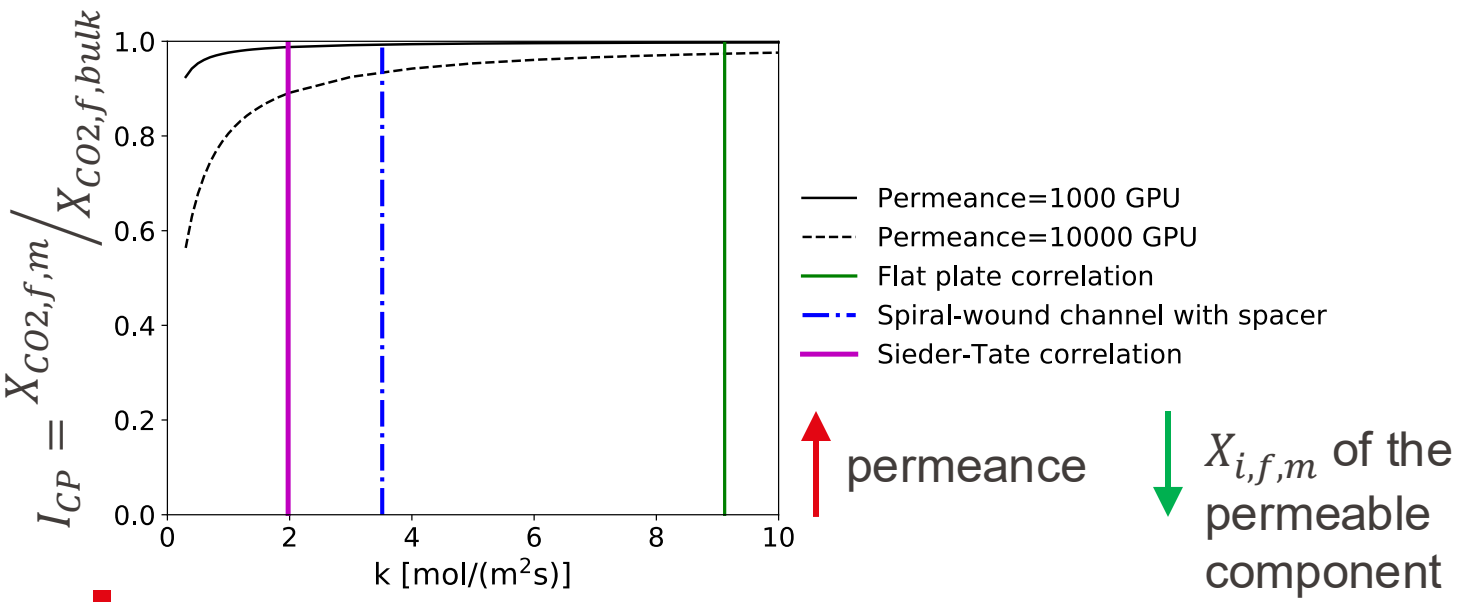
Mass transfer coefficient

Sherwood number Diffusion coefficient

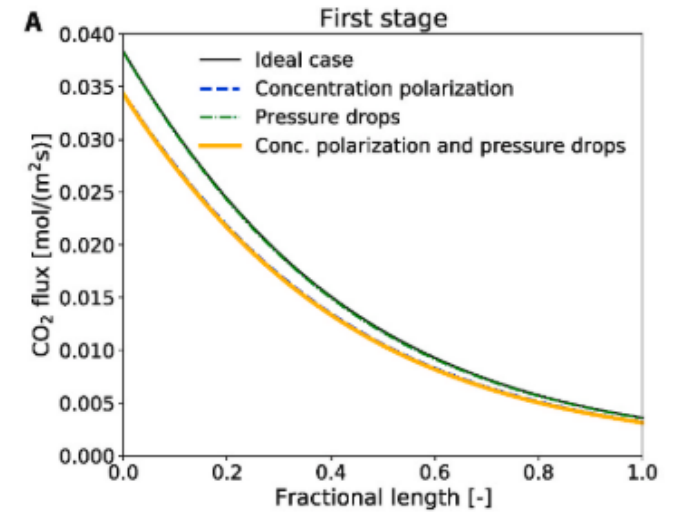
$$k = \left(\frac{Sh D}{d_{hydr}} \right) \frac{P_{feed}}{R T_{feed}}$$

Hydraulic diameter of the channel

$Sh = 0.664 Re^{0.5} Sc^{0.33}$	Boundary layer over a flat plate
$Sh = 0.2 Re^{0.57} Sc^{0.4}$	Channels with spacers in spiral-wound modules
$Sh = 1.86 \left(Re Sc \frac{d_{hydr}}{L} \right)^{1/3}$	Flow in round tubes (Sieder-Tate)



Impact of non ideal effects on the flux



Dimensionless numbers

Reynolds number

$$Re = \frac{\rho v d_{hydr}}{\mu}$$

Schmidt number

$$Sc = \frac{\mu}{\rho D}$$

Sherwood number

$$Sh = \frac{k}{D/d_{hydr}}$$

$$Sh = A Re^a Sc^b$$