Membrane processes for gas separation

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Lecture 7

29.10.2024

Reference book: Membrane Technology and Applications, R. W. Baker, Wiley 2012 (3rd ed.)

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

Agenda

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

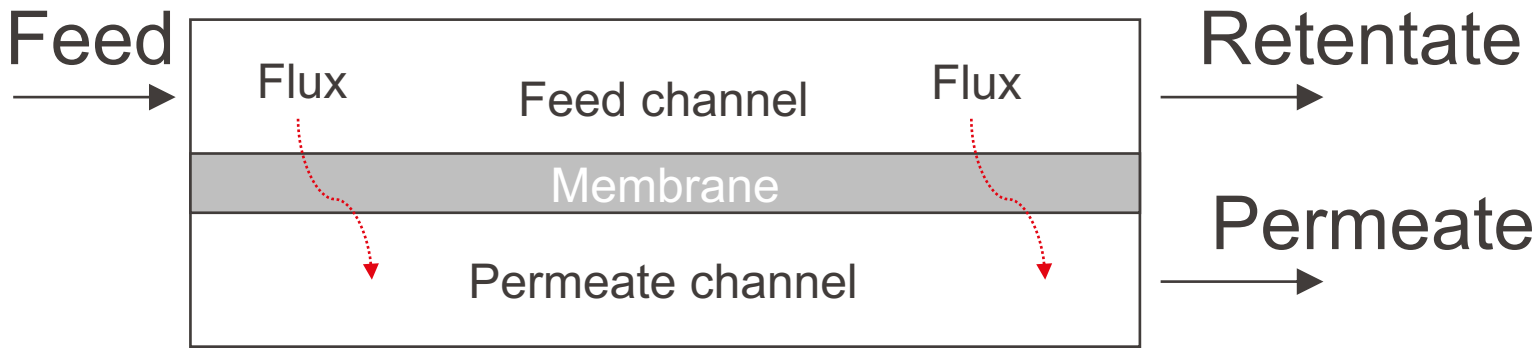
✓Simulations

Group projects presentations on 12.11

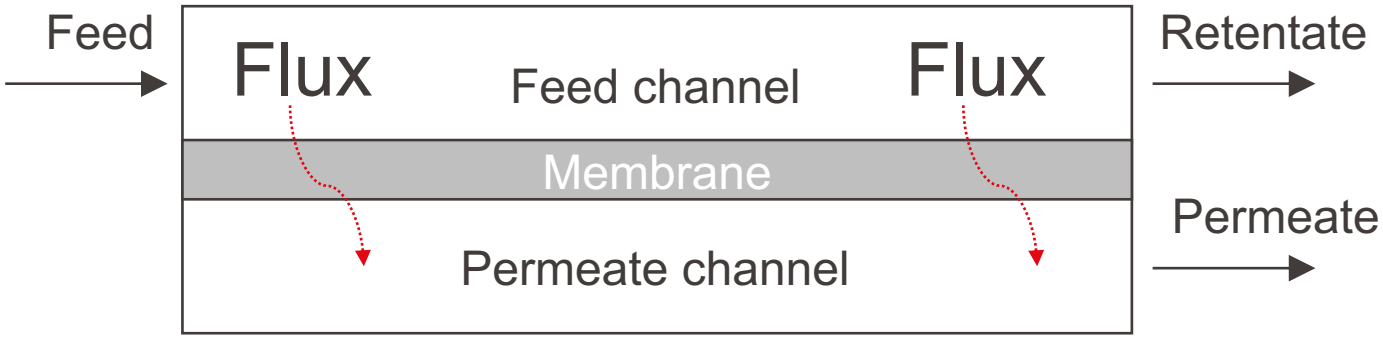
- Groups of 3 students (11-12 groups) → ~ 12 minutes per group (presentation + questions)

- 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



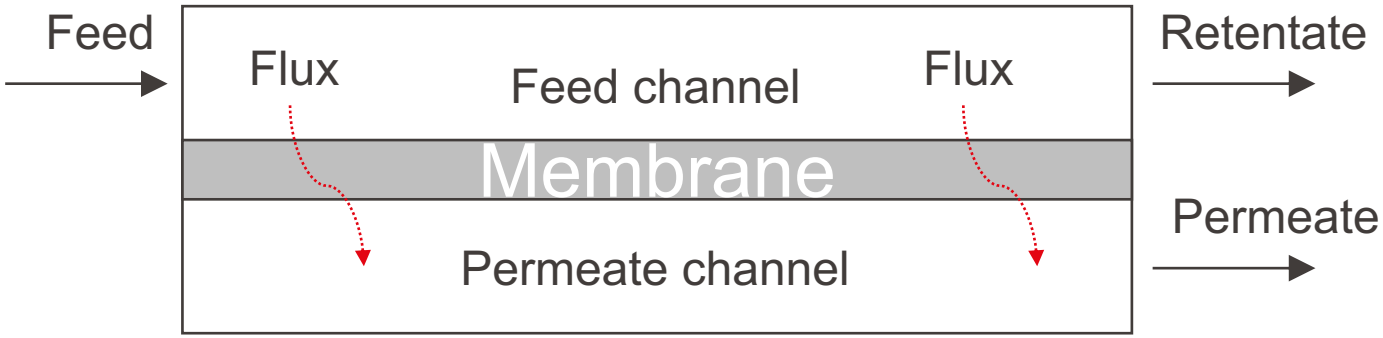
Membrane module, definitions



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

= *Mass transfer coefficient* × *chemical potential gradient*

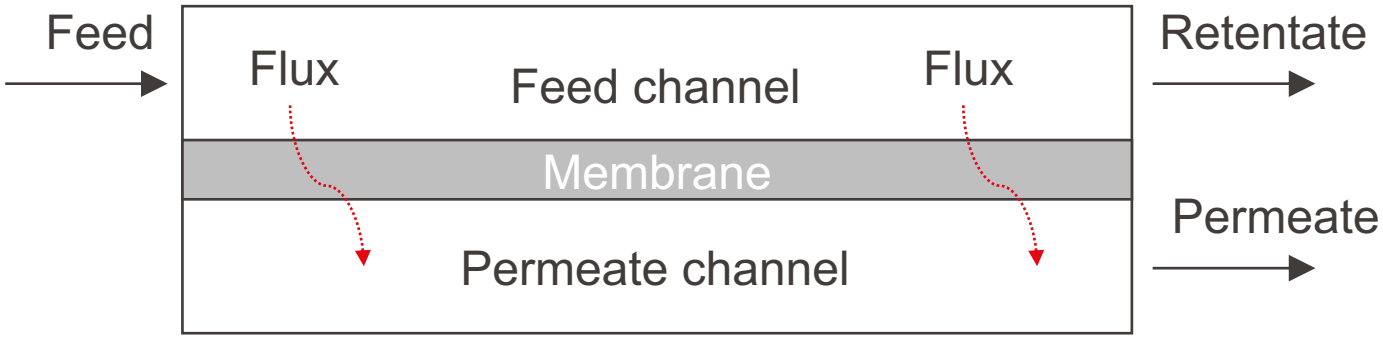
Membrane module, definitions



- ✓ **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 = $\frac{Permeance\ A}{Permeance\ B}$

Membrane module, definitions

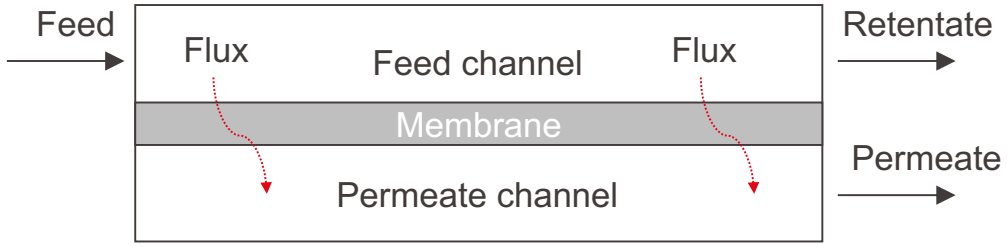


Outputs

- ✓ **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*

$$X_{i,f}Q_f = X_{i,r}Q_r + X_{i,p}Q_p \qquad \sum X_{i,f} = \sum X_{i,r} = \sum X_{i,p} = 1$$

- 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

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

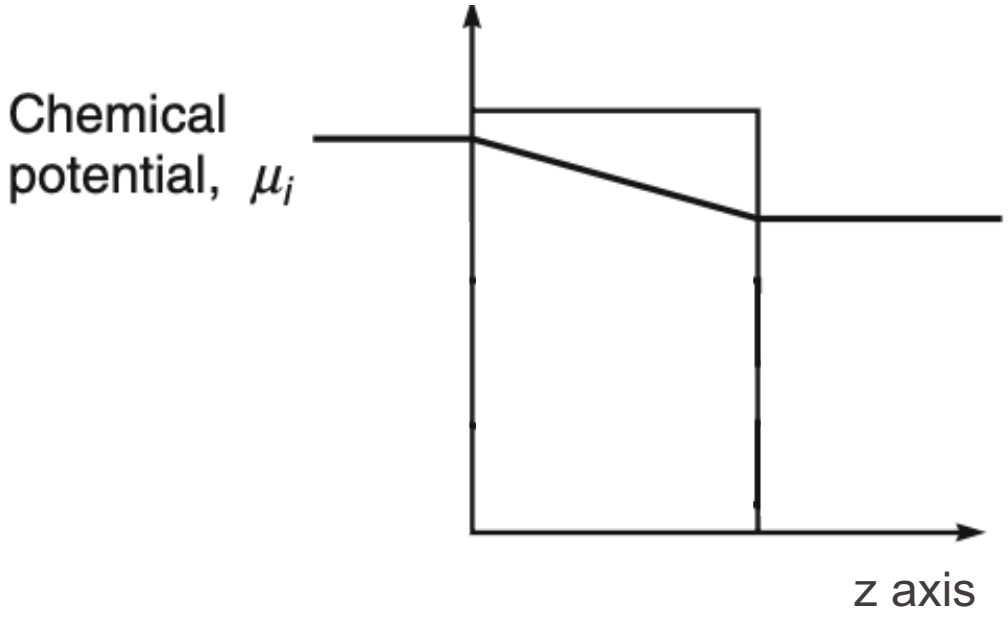
How do we calculate J?

Transport mechanism through the membrane

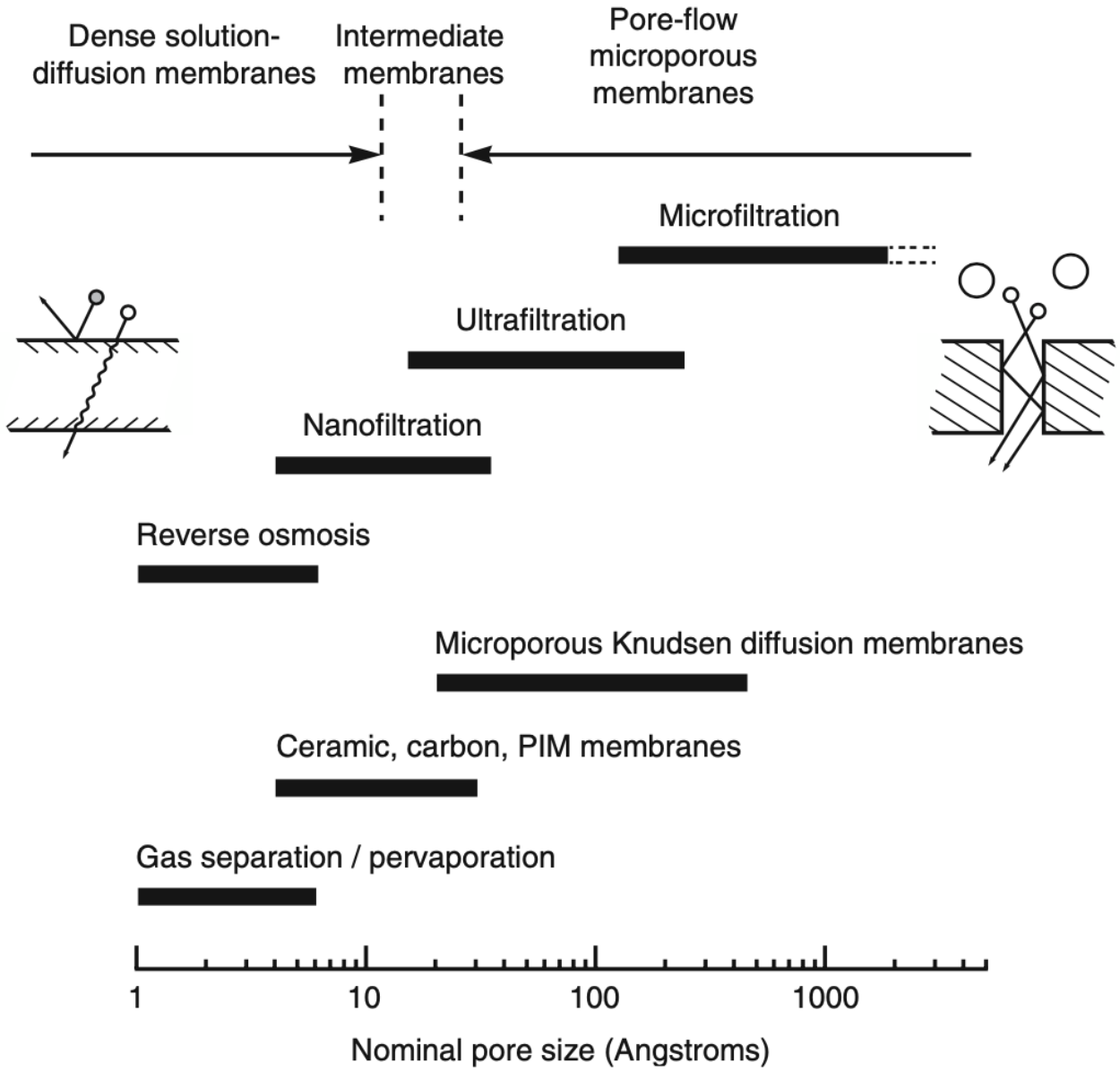
- Generic definition of the flux as function of chemical potential gradient

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

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

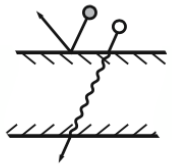


Transport mechanism through the membrane



Transport mechanism through the membrane

Dense membranes

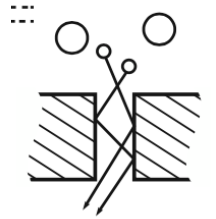


Flux driven by the **concentration gradient**

Transport based on solution-diffusion

Selectivity based on solubility and diffusivity

Porous membranes



Flux driven by the total **pressure gradient**

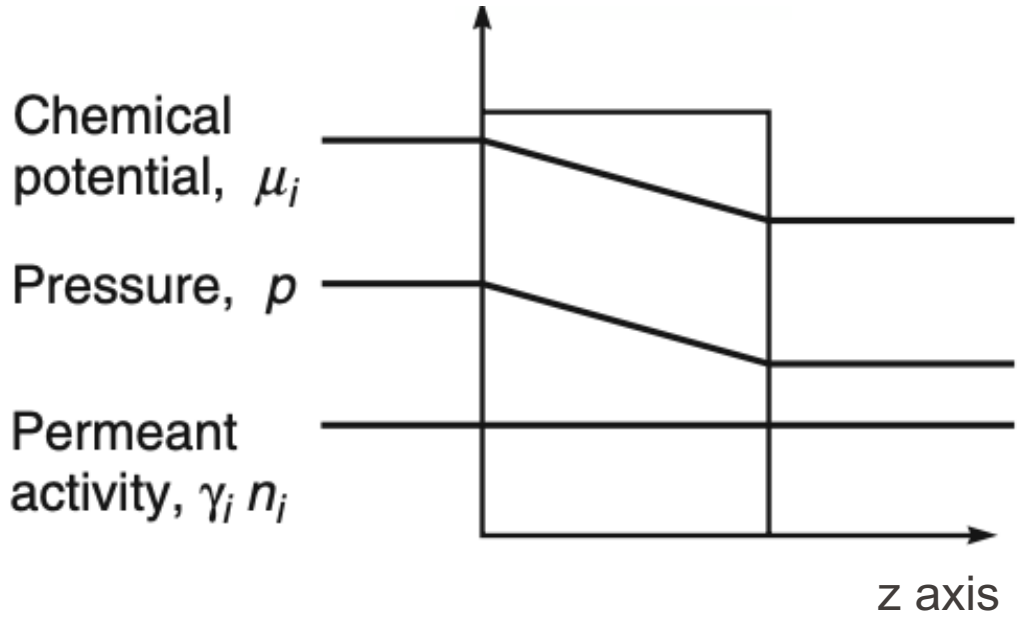
Transport based on viscous flow and diffusion

Selectivity based on pore size

Transport mechanism through the membrane

Porous membranes

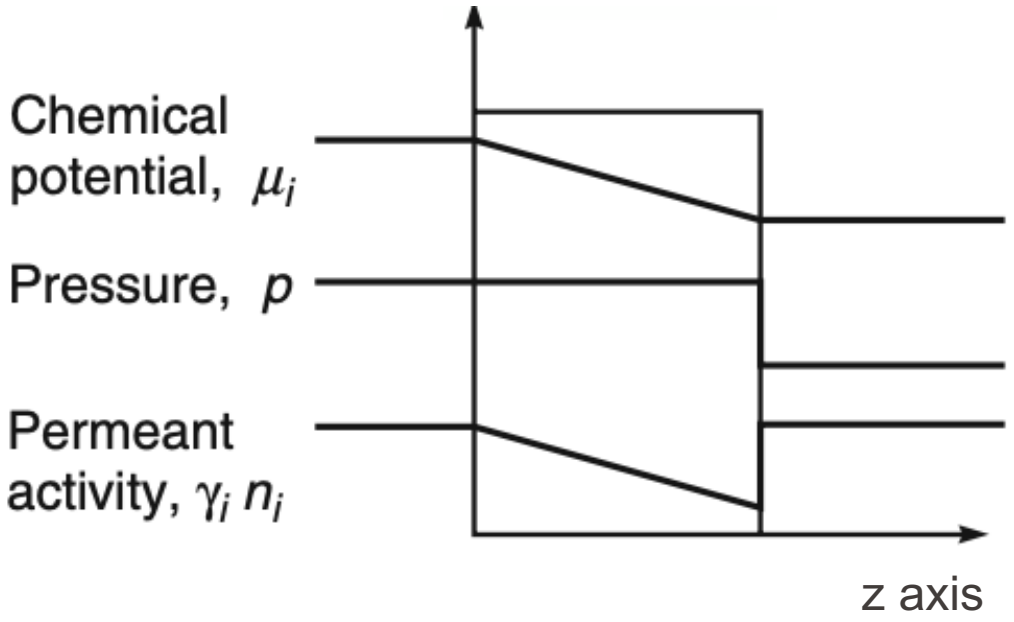
- Pore-flow model assumes that concentration is uniform within the membrane -> only pressure gradient



Transport mechanism through the membrane

Dense membranes

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



Solution-diffusion model for dense membranes

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

uniform pressure

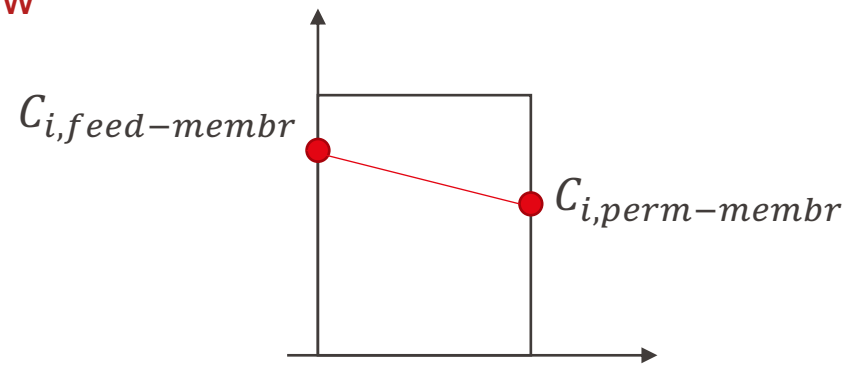
When we refer to the concentration C_i [kg/m^3]

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

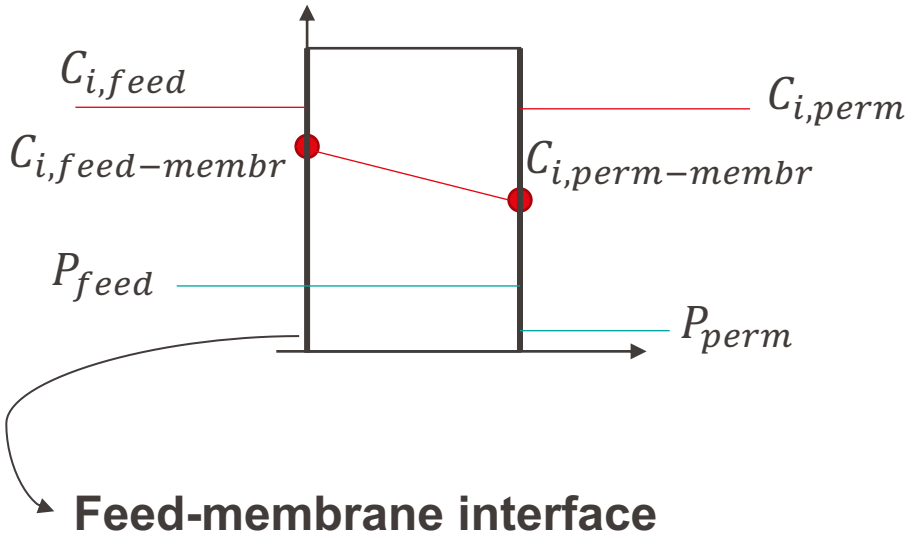
same form as the Fick's law

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

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

$p_{i,feed}$

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

$C_i = m_i \rho_m X_i$

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

$K_{i,G}$

Flux from solution-diffusion model in gas separation

Feed-membrane interface

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

Permeate-membrane interface

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

v_i molar volume in the membrane material

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

Poynting correction ~ 1

Partial pressure difference across the membrane

Total pressure on the feed side

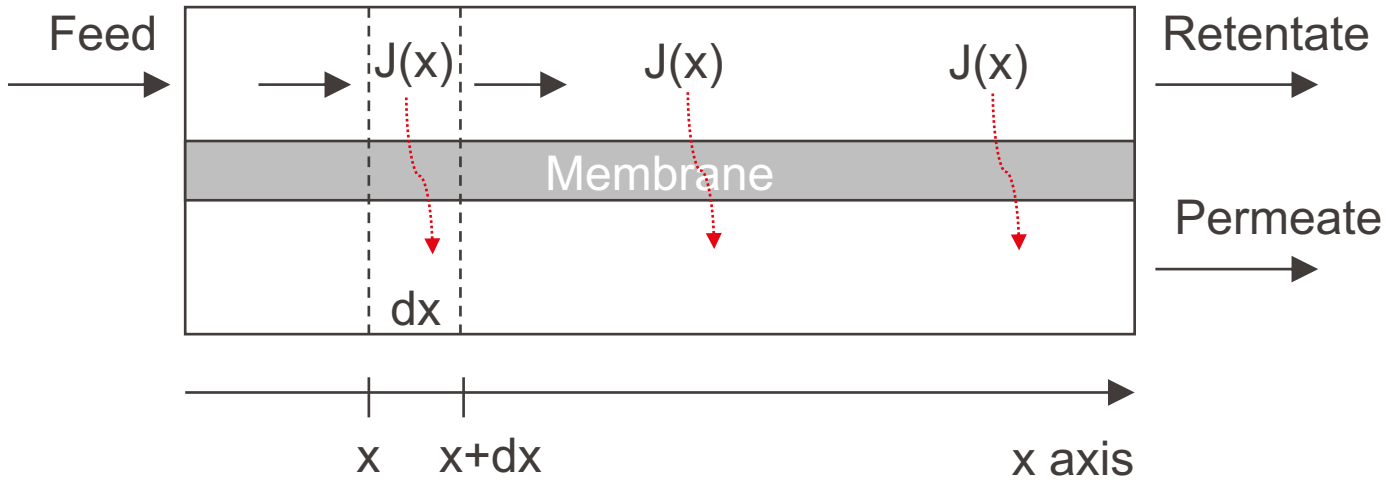
$$J_i = \frac{D_i K_{i,G}\left(p_{i,feed} - p_{i,perm}\right)}{l} = \frac{P_{i,G}\left(p_{i,feed} - p_{i,perm}\right)}{l}$$

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

Modelling a membrane module

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

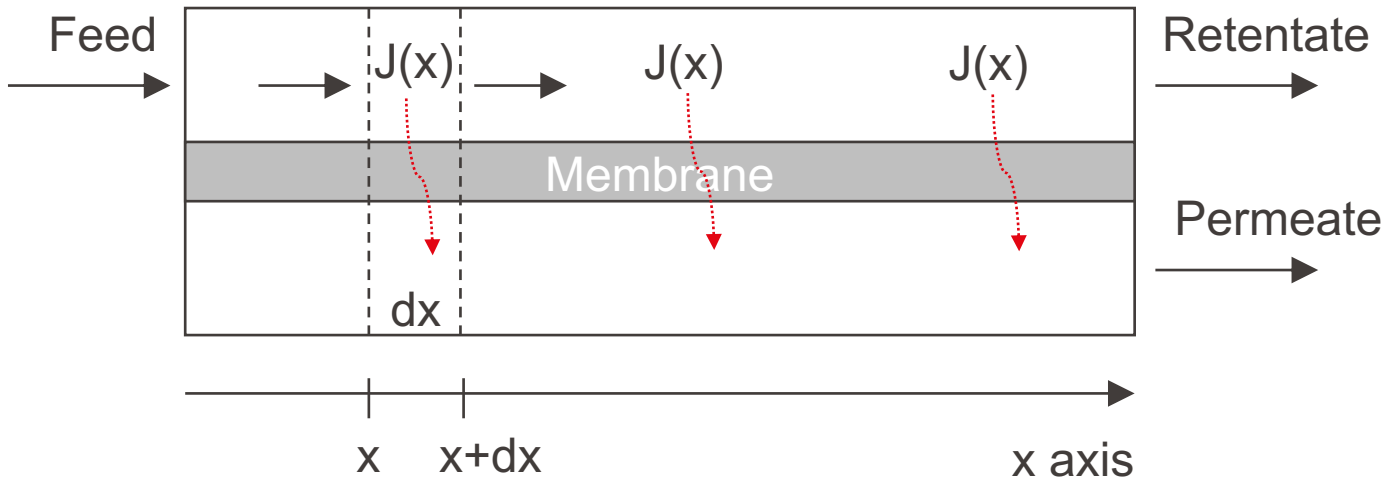
$$J_i(x) = \frac{P_{i,G}\left(p_{i,feed}(x) - p_{i,perm}(x)\right)}{l} = \boldsymbol{P}_i\left(P_{feed}\, X_{i,feed}(x) - P_{perm}\, X_{i,perm}(x)\right)$$

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

Modelling a membrane module

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

Co-current flow arrangement



$$J_i(x) = \frac{P_{i,G}\left(p_{i,feed}(x) - p_{i,perm}(x)\right)}{l}$$
$$= \boldsymbol{P}_i\left(P_{feed}\, X_{i,feed}(x) - P_{perm}\, X_{i,perm}(x)\right)$$

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

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
$J_i(x) = \boldsymbol{P}_i \left(P_{feed}\, X_{i,feed}(x) - P_{perm}\, X_{i,perm}(x) \right)$	$N_{components} \times N_{elem}$
$J(x) = \sum_{components} J_i(x)$	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 $N_{components}$ × N_{elem} + 4 N_{elem}

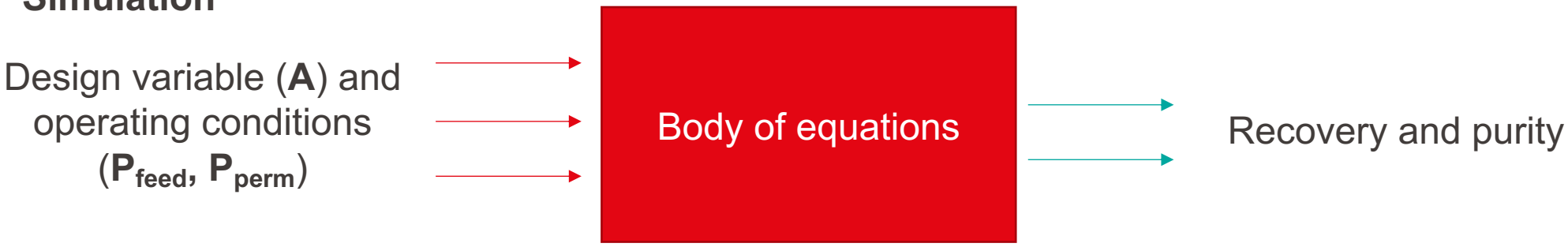
Variable	N variable
$J_i(x)$	$N_{components} \times N_{elem}$
$J(x)$	N_{elem}
$Q_r(x)$	N_{elem}
$X_{i,r}(x)$	$N_{components} \times N_{elem}$
$Q_P(x)$	N_{elem}
$X_{i,p}(x)$	$N_{components} \times N_{elem}$
$Q_f(x)$	N_{elem}
$X_{i,f}(x)$	$N_{components} \times N_{elem}$
	total: 4 $N_{components}$ × N_{elem}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

For given $\mathbf{P_{feed}}$, $\mathbf{P_{perm}}$ and **A**

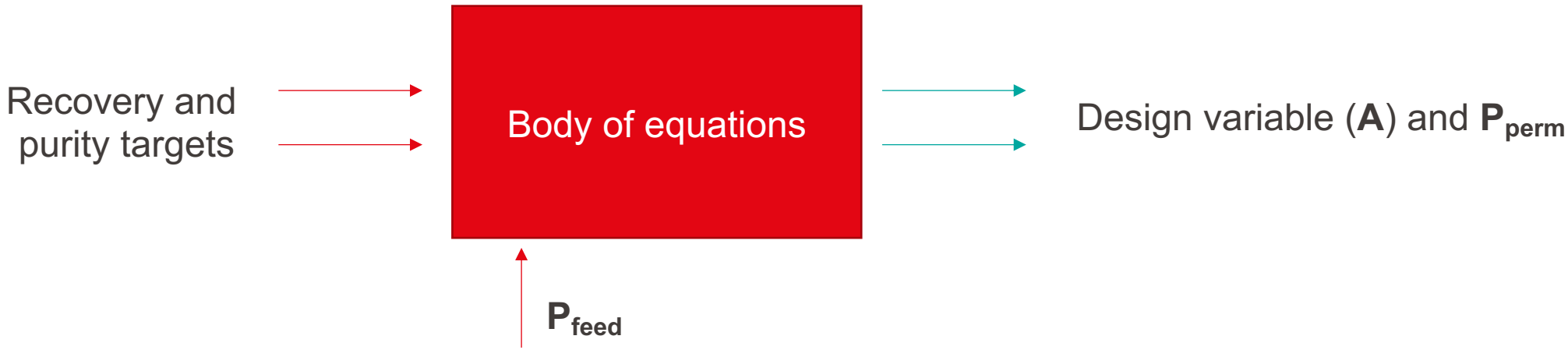
$N_{equations} = N_{variables}$

Modelling approaches

Simulation

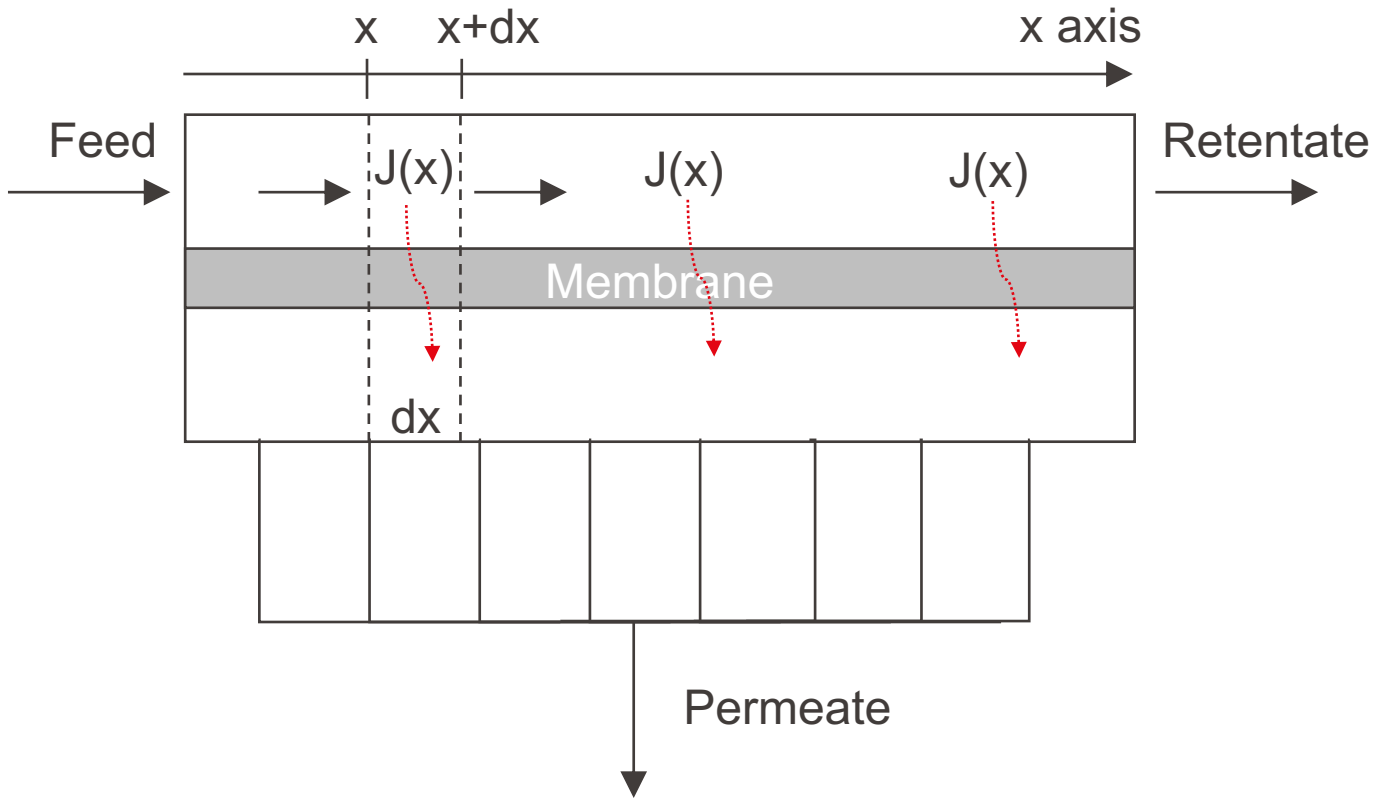


Design



Membrane module: flow arrangements

Cross-current flow arrangement



No mixing in the permeate channel

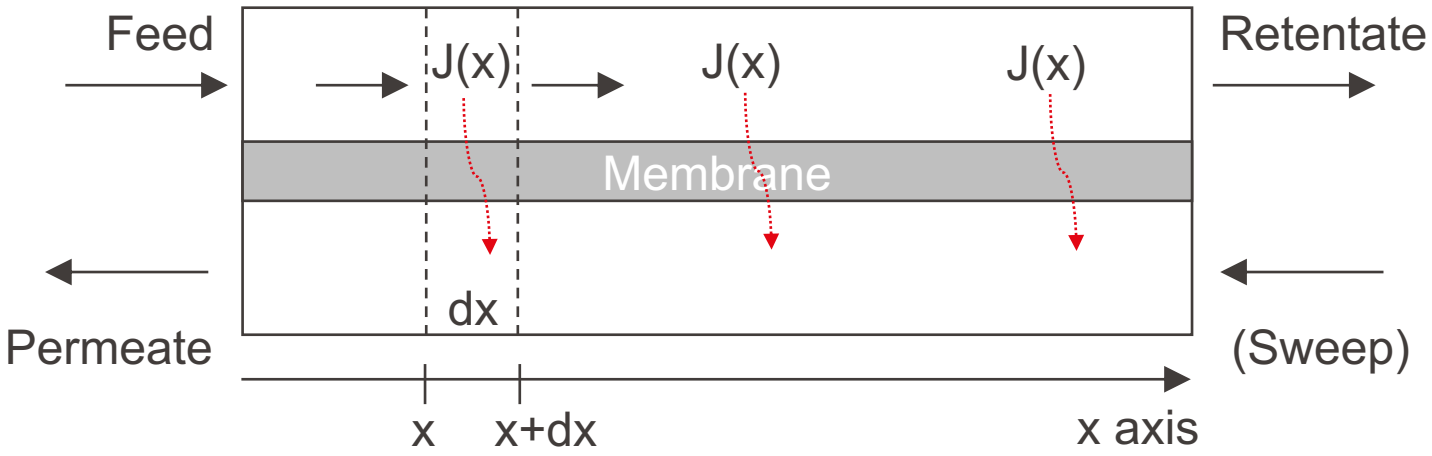
$$J_i(x) = \frac{P_{i,G}\left(p_{i,feed}(x) - p_{i,perm}(x)\right)}{l}$$
$$= \boldsymbol{P}_i\left(P_{feed}\, X_{i,feed}(x) - P_{perm}\, \boldsymbol{X'_{i,perm}}(\boldsymbol{x})\right)$$

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

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

Membrane module: flow arrangements

Counter-current flow arrangement



$$J_i(x) = \frac{P_{i,G}\left(p_{i,feed}(x) - p_{i,perm}(x)\right)}{l}$$
$$= \boldsymbol{P}_i\left(P_{feed}\, X_{i,feed}(x) - P_{perm}\, X_{i,perm}(x)\right)$$

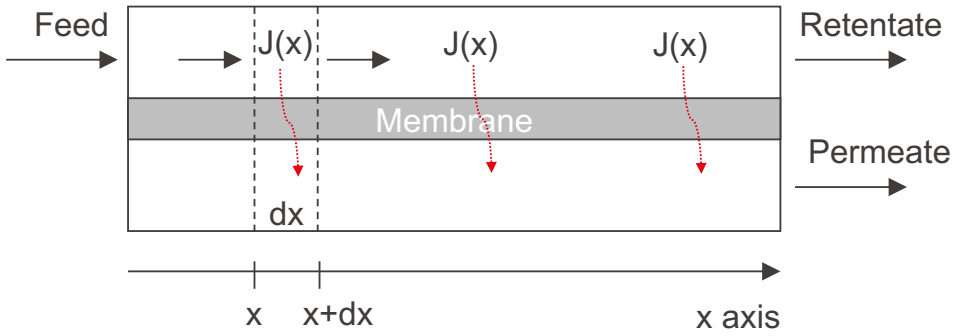
Permeate side

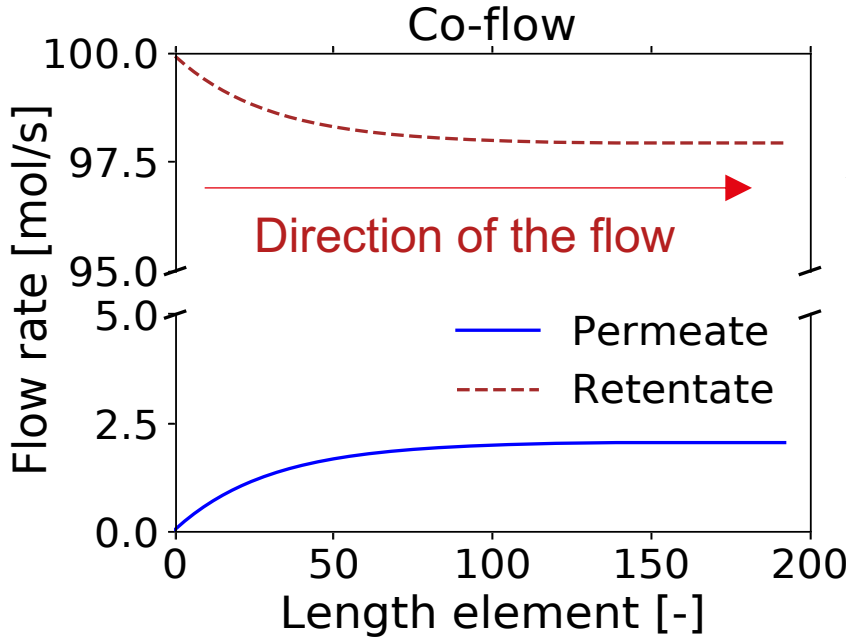
$$Q_p(x) = Q_p\,(x + dx) + J(x)\, dA$$

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

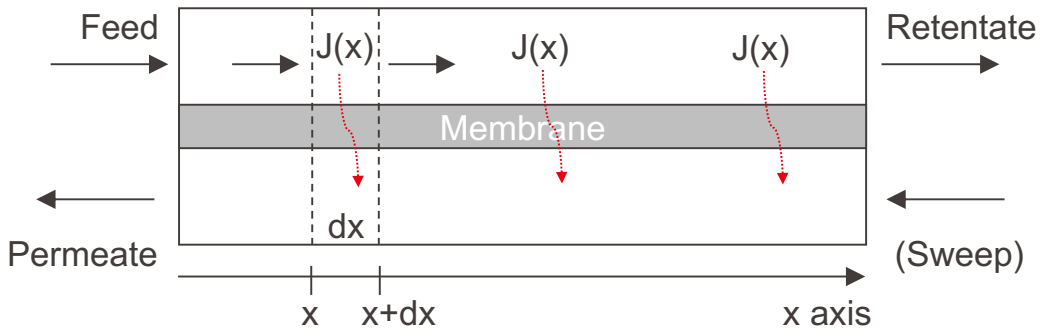
Profiles along the membrane module

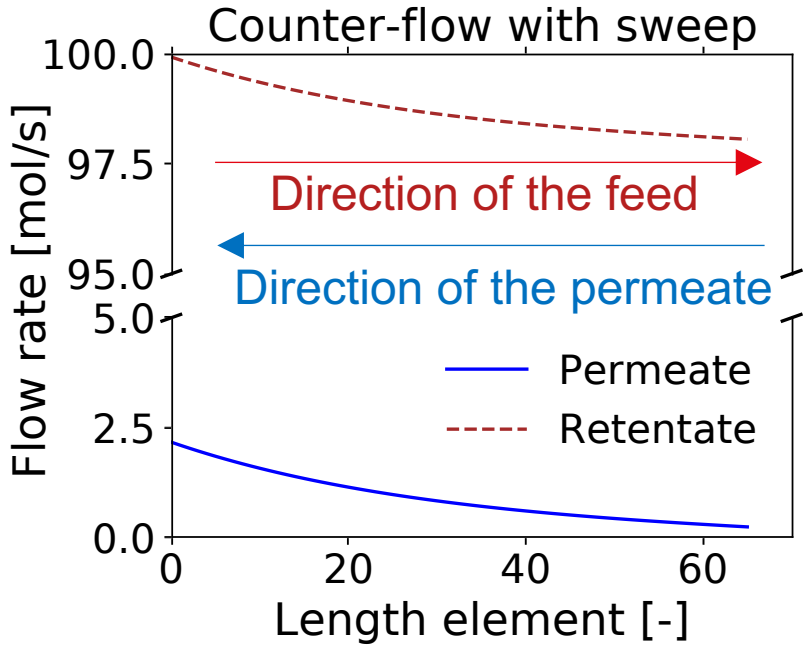
Co-current flow arrangement





Counter-current flow arrangement





- **Reduced driving force along the length**

Almost constant driving force along the length

Multi-stage configurations

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})

$$J_i(x) = \boldsymbol{P}_i \left(P_{feed}\, X_{i,feed}(x) - P_{perm}\, X_{i,perm}(x) \right) > 0 \text{ if } \frac{P_{feed}}{P_{perm}} > \frac{X_{i,perm}}{X_{i,feed}}$$

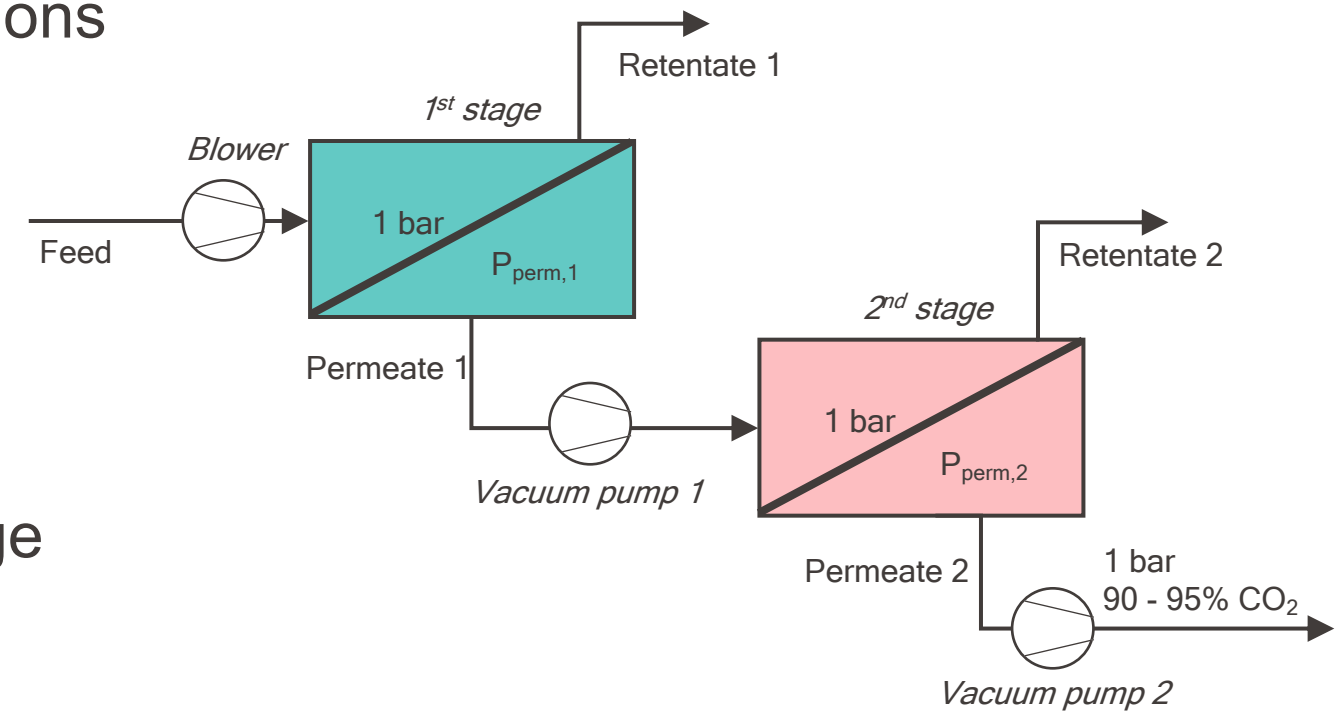
Max separation limited by pressure ratio

Alternative: multi-stage configurations

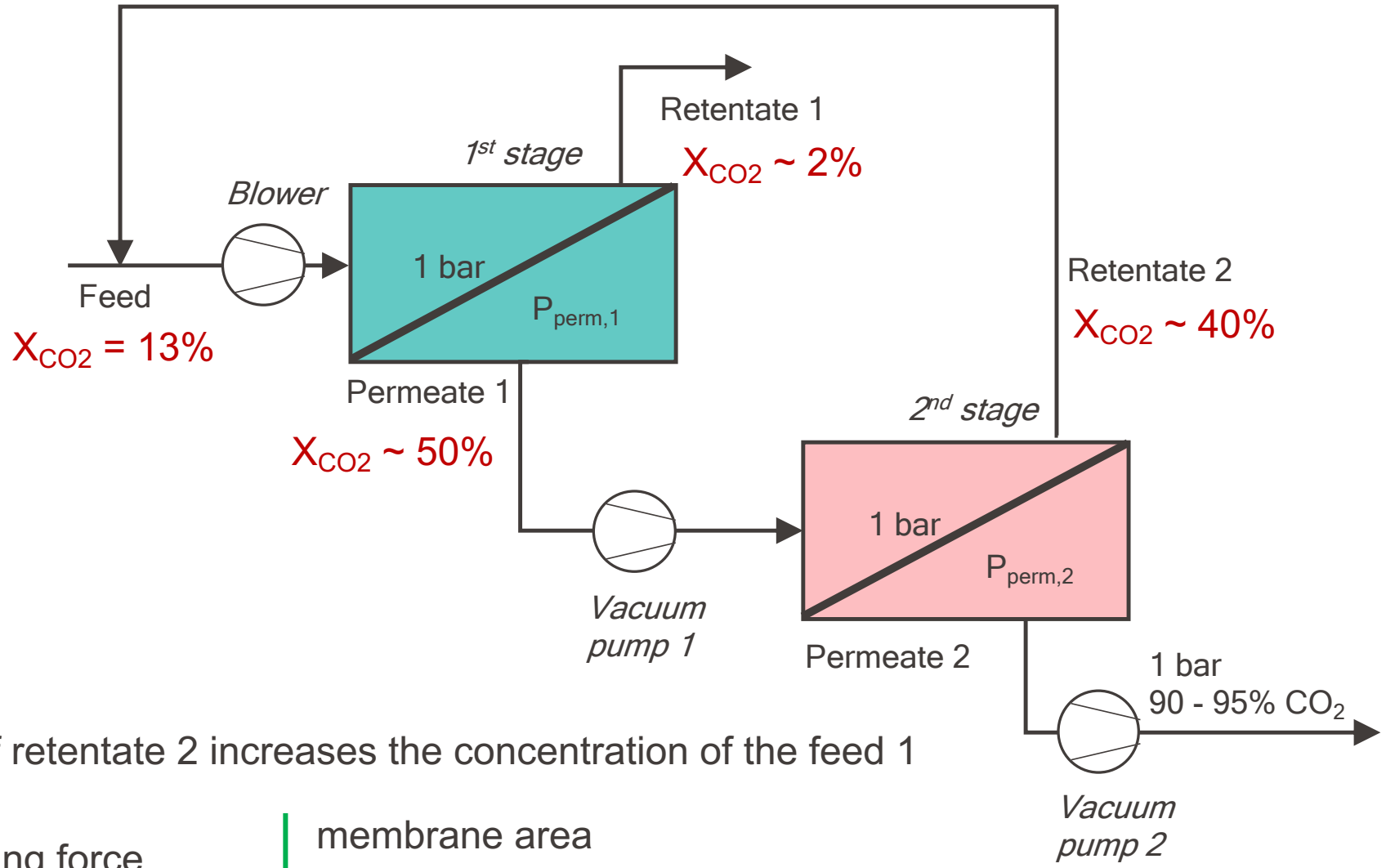
$$Q_{feed,2} = Q_{perm,1}$$

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

Higher driving force in the 2nd stage



Recycle design



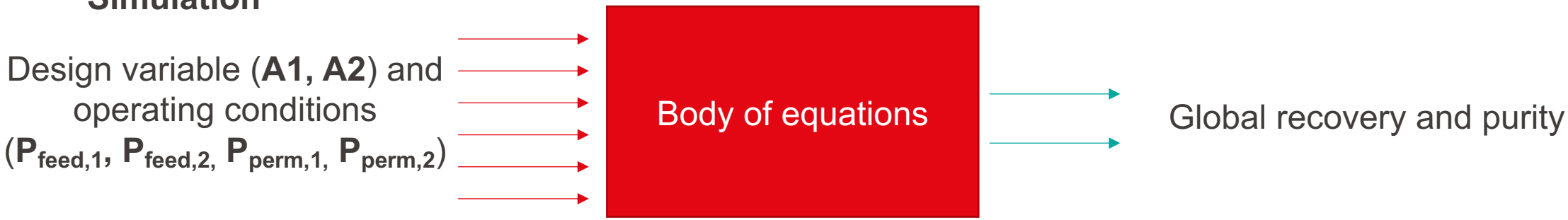
Recycle of retentate 2 increases the concentration of the feed 1

↑ driving force

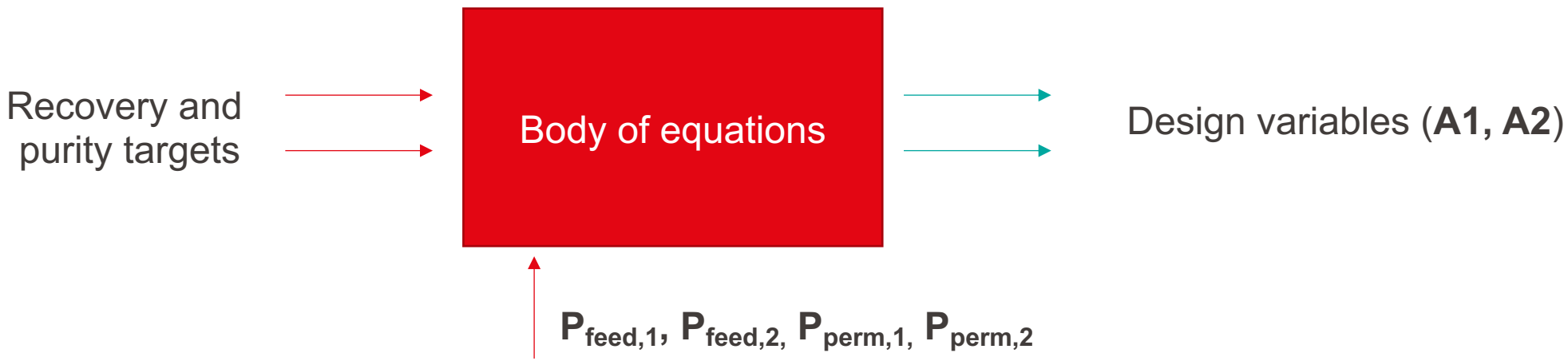
↓ membrane area
energy

Modelling approaches

Simulation



Design



Agenda

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 mol/(m^2sPa)]
- 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):

$$X'_{CO2,p}[i] = \frac{1+(\alpha-1)(\beta+X_{CO2,f}[i])-\sqrt{[1+(\alpha-1)(\beta+X_{CO2,f}[i])]^2-4\alpha\beta(\alpha-1)X_{CO2,f}[i]}}{2\beta(\alpha-1)}$$

$$J_{CO2}[i] = \boldsymbol{P}_{CO2}\left(P_{feed}\, X_{CO2,f}[i] - P_{perm}\, \boldsymbol{X'_{CO2,p}}[i]\right)$$

$$J_{N2}[i] = \boldsymbol{P}_{N2}\left(P_{feed}\, X_{N2,f}[i] - P_{perm}\left(1 - \boldsymbol{X'_{CO2,p}}[i]\right)\right)$$

$$Q_r[i] = Q_f[i] - (J_{CO2}[i] + J_{N2}[i])\, dA$$

$$X_{CO2,r}[i]\, Q_r[i] = X_{CO2,f}[i]\, Q_f[i] - (J_{CO2}[i])\, dA$$

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

α selectivity

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

Output: $Q_{ret,out} = Q_r[-1]$ $\quad X_{CO2,ret\ out} = X_{CO2,r}[-1]$ $\quad Recovery = \frac{Q_{perm,out} X_{CO2,perm\ out}}{X_{f,CO2}[0] Q_f[0]}$

$Q_{perm,out} = Q_f[0] - Q_{ret,out}$ $\quad X_{CO2,perm\ out} = Purity = \frac{X_{f,CO2}[0] Q_f[0] - X_{CO2,ret\ out} Q_{ret,out}}{Q_{perm,out}}$

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, Sel = 30

Standard set: Pf = 1 bar, Pp = 0.1 bar, Xf = 0.1, Qf=2.5 mol/s, A = 10 m^2

-> 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
- Xf: 0.01 – 0.5
- Permeance: 1000 – 10000 GPU
- Selectivity: 20-100

Validity range Double stage

Permeance = 10000 GPU, SeI = 30

Standard set: Pf1 = 1 bar, Pp1 = 0.1 bar, Pf2 = 1 bar, Pp2 = 0.2 bar,
Xf = 0.1, Qf = 2.5 mol/s, A1 = 10 m^2, A2 = 5 m^2

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

- A membrane1: 5 - 50 m2 , A membrane 2: 1 - 10 m2
- P permeate 1, P permeate 2: 0.01 – 0.5 bar
- Pfeed1, Pfeed2: 1–5 bar
- Qfeed: 1 – 100 mol/s
- Xf: 0.01 – 0.5
- Permeance: 1000 – 10000 GPU
- Selectivity: 20-100

Group projects

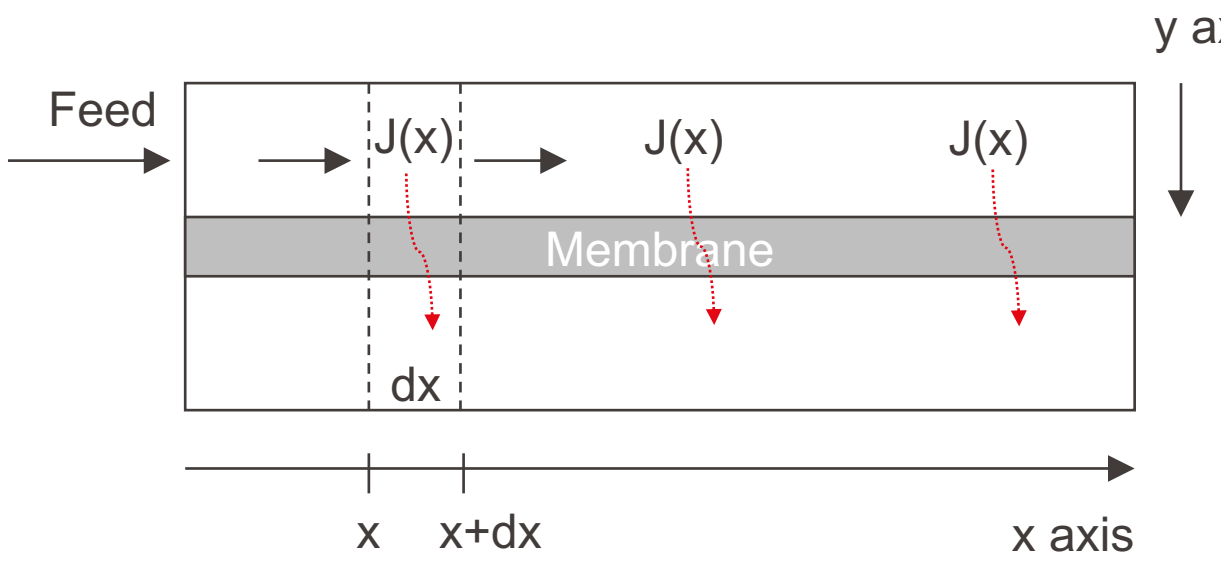
- Group 1: influence of **feed flow rate** on single and double stage
- Group 2: influence of **feed concentration** on single and double stage
- Group 3: influence of **feed pressure** on single stage and **feed pressure 1** on double stage
- Group 4: influence of **feed pressure** on single stage and **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 11: influence of **permeance of stage 1 and stage 2** of the double stage (varied independently)
- Group 12: influence of **selectivity of stage 1 and stage 2** of the double stage (varied independently)

Group projects presentations on 12.11

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

- global recovery and purity variation with the given parameter (e.g., permeance)
- profiles of CO_2 concentration in the feed and permeate channel with 2-3 values of the given parameter in the investigated range
- profiles of CO_2 and N_2 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

Non-ideal phenomena



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

Concentration polarization → decrease of $X_{i,feed}$ along the y axis

$$J_i(x) = \frac{P_{i,G}\left(p_{i,feed}(x) - p_{i,perm}(x)\right)}{l} = \boldsymbol{P}_i\left(P_{feed}\, X_{i,feed}(x) - P_{perm}\, X_{i,perm}(x)\right)$$

Non-ideal phenomena
Pressure drops in the feed channel

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

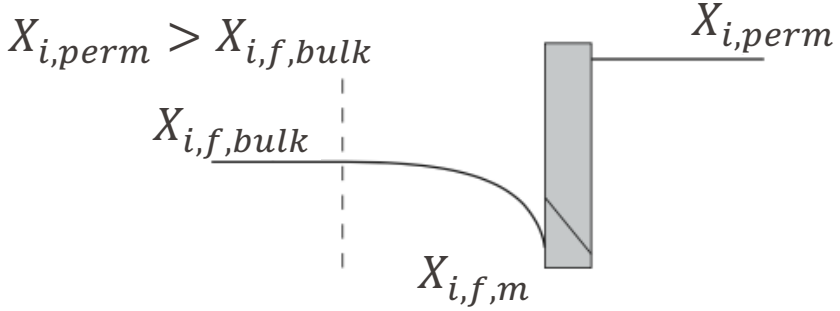
$$\frac{dP_{feed}}{dx} = -f \frac{\rho}{2\, d_{hydr}} v^2$$

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

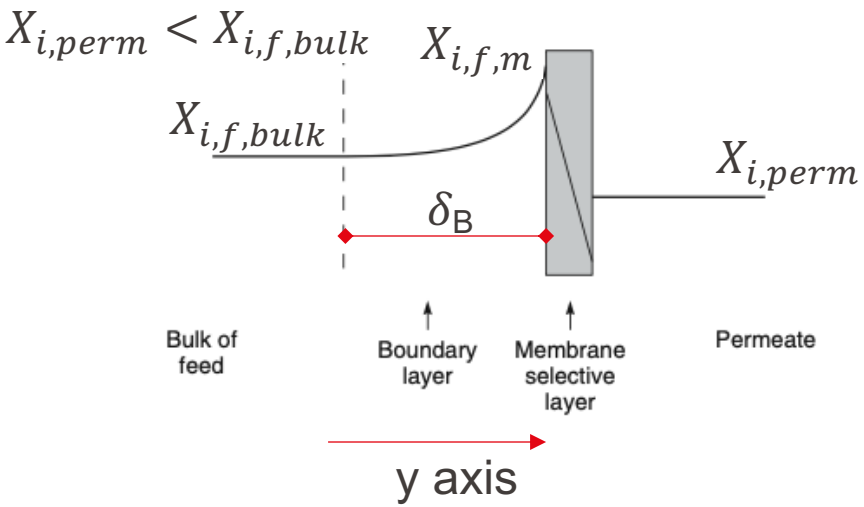
Common limit on pressure drops for channel design: 1.5 psi/m (0.1 bar/m)

Non-ideal phenomena
Concentration polarization

More permeable component



Less permeable component



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

For a binary mixture and cross-current flow arrangement:

$$J_1 = \boldsymbol{P}_1\left(P_{feed}X_{1,f,m} - P_{perm}\,X'_{1,perm}\right)$$

$$J_2 = \boldsymbol{P}_2\left(P_{feed}\left(1 - X_{1,f,m}\right) - P_{perm}\left(1 - X'_{1,perm}\right)\right)$$

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

mass transfer coefficient k

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

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

Concentration polarization
Mass transfer coefficient

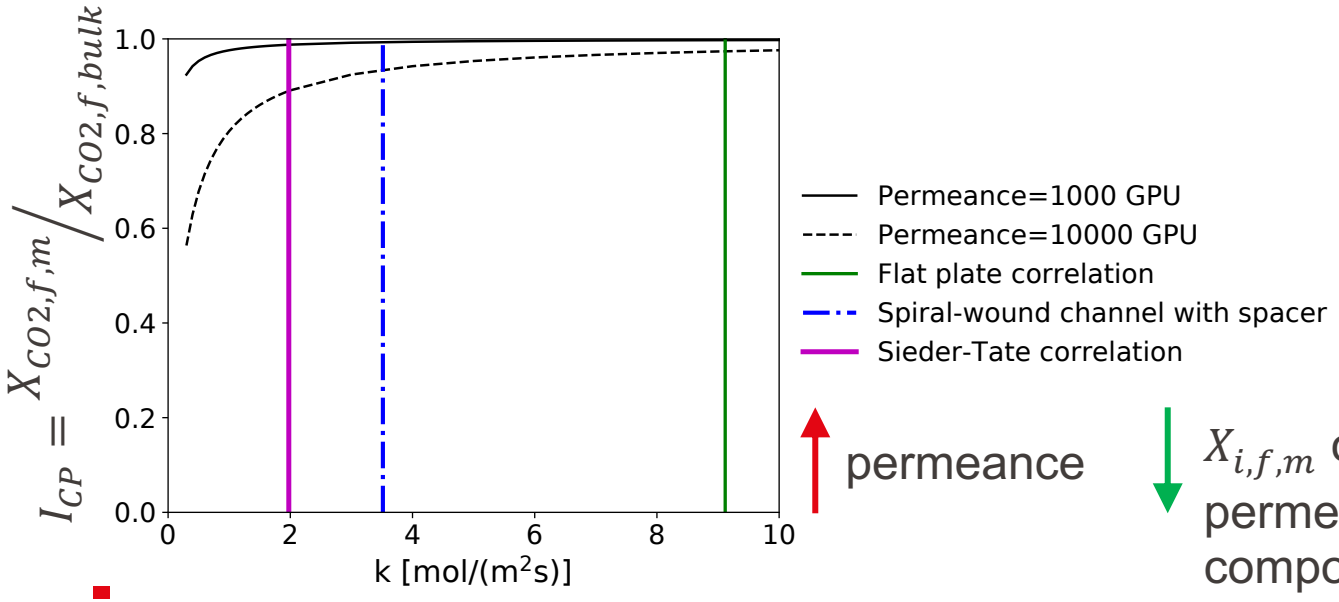
Sherwood number

Diffusion coefficient

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

Hydraulic diameter of the channel

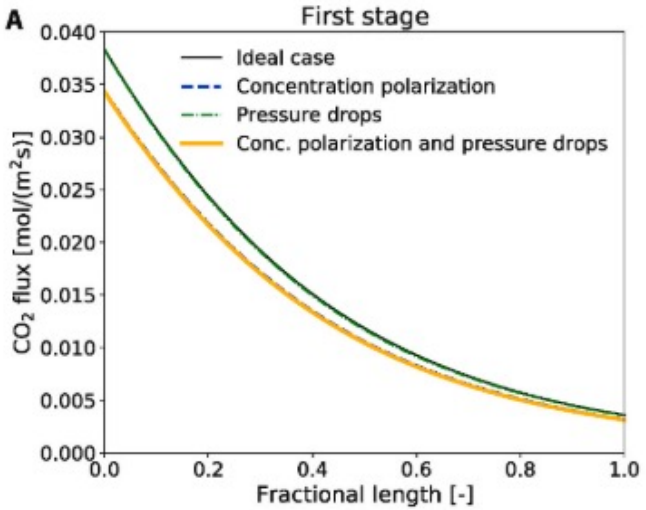
$Sh = 0.664\ Re^{0.5}\ Sc^{0.33}$	Boundary layer over a flat plate
$Sh = 0.2\ Re^{0.57}\ Sc^{0.4}$	Channels with spacers in spiral-wound modules
$Sh = 1.86 \left(Re\ Sc\ \frac{d_{hydr}}{L}\right)^{1/3}$	Flow in round tubes (Sieder-Tate)



permeance

$X_{i,f,m}$ of the permeable component

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

$$Sh = A \, Re^{a} \, Sc^{b}$$