

Membrane processes

Separation of liquid or gaseous mixtures by mass transport through membrane (= permeation). Membrane is **selective**, i.e. it has different permeability for different components. Conditions for separation on membrane are either **hydromechanical** (similar to filtration) or **diffusion-based**.

Membranes can be:

- **porous** – transport is via diffusion or by pressure difference
- **nonporous** – dissolution + diffusion

Membrane are made of:

- natural products: **acetyl-cellulose**
- synthetic: **cross-linked polymers**
- other materials: **ceramics, metals**

Asymmetric membranes: thin skin (actual membrane) is attached to a thick, porous and sturdy support → resistance to large pressure differences

Some types of membrane processes

- **micro + ultra filtration (UF):** Analogous to filtration driving force is pressure difference (hydrodynamical process) up to 1 MPa. Separation of suspensions and colloids with particles of 10^{-1} – 10^{-3} μm .
- **reverse osmosis (RO):** Also hydromechanical process with pressure differences up to 10 MPa. Separation of components from true solutions (desalination of water)
- **gas permeation:** Separation of gaseous mixtures by diffusion driven by partial pressure difference. Air separation, gas cleaning.
- **pervaporation:** Separation of liquid solutions by diffusion; mixture evaporates after passing through the membrane
- **dialysis:** Diffusion driven transport in solution. Used in medicine → artificial kidney
- **electrodialysis:** Driving force is electric potential difference (voltage); desalination of water

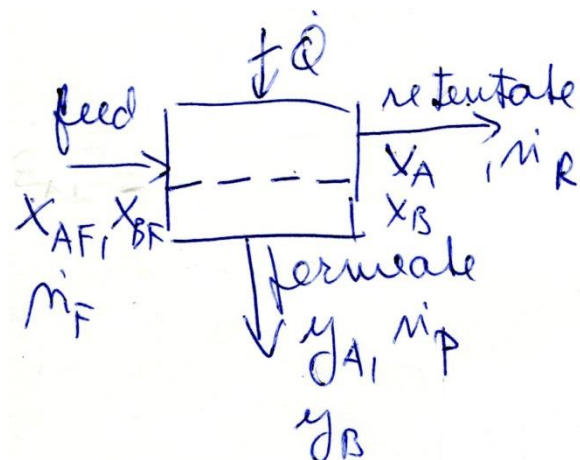
Membrane modules

- **tubular** – a tube or capillary of diameter 10^{-1} – 10^1 mm, easy to clean, low performance per volume of the module; use for UF
- **plate-and-frame** – like filter press, i.e. a series of flat membrane sheets stacked one above another and separated by spacers; advantage – can be cleaned
- **spiral wound** – plate-and-frame rolled into a cylinder → high surface to volume ratio; use for all membrane processes
- **hollow fibers** – thin fibers placed in a shell → high surface to volume ratio; used for all membrane processes

Balance of membrane modules

We assume two components:

- A ... solute (or dispersed component)
- B ... solvent (or dispergant)



Balance on moles

- total: $\dot{n}_F = \dot{n}_R + \dot{n}_P$
- component A: $\dot{n}_F x_{AF} = \dot{n}_R x_A + \dot{n}_P y_A$
 $x_{AF} = (1 - \theta)x_A + \theta y_A$, where $\theta = \frac{\dot{n}_P}{\dot{n}_F}$ is called **cut**
- component B: $x_{BF} = (1 - \theta)x_B + \theta y_B$

Enthalpy balance

$$h_F + \frac{\dot{Q}}{\dot{n}_F} = (1 - \theta)h_R + \theta h_P$$

h ... molar enthalpy

The area of the membrane is then calculated from

$$\dot{n}_P y_k = \Phi_k A \text{ where } k = A \text{ or } B$$

Φ_k is the **flux** which can express (see later)

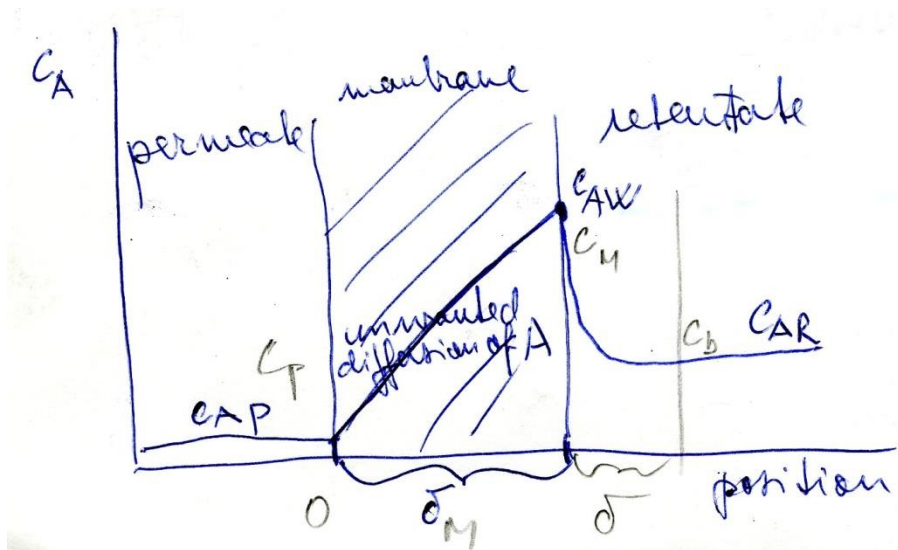
Concentration polarization

Occurs in membrane separation of liquids when using pressure difference (RO, UF). Component A (solute) tends to accumulate at the membrane, its concentration there is high \rightarrow A leaks through the membrane by diffusion because of and increased driving force $c_{AW} - c_{Ap}$ could be counteracted by stirring.

A measure of quality of the membrane is **rejection coefficient**:

$$R = \frac{c_{AR} - c_{Ap}}{c_{AR}}$$

$$M = \frac{c_{AW}}{c_{AR}} \dots \text{polarization modulus}$$



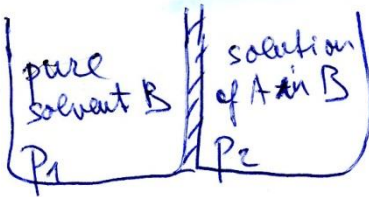
Kinetics of some membrane processes

Generally, kinetics of transport through membrane is formulated as follows:

$$\text{flux} = \frac{\text{permeability}}{\text{thickness}} \times \text{driving force}$$

$$\text{flux} = \frac{\text{flow}}{\text{area}}; \text{flow can be } [\text{m}^3 \text{ s}^{-1}] \text{ or } [\text{mol s}^{-1}]$$

Kinetics for RO

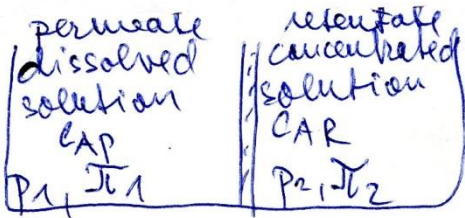


$$\Delta p = p_2 - p_1$$

Membrane is permeable for B only

- osmosis** – flow of B into the solution if $\Delta p < \pi$
- equilibrium** is reached after osmosis increases p_2 so that $\Delta p = \pi$... **osmotic pressure**
- reverse osmosis** – if p_2 is increased (by pump or hydrostatic pressure) so that $\Delta p > \pi$

In a real membrane (rejection coefficient $R < 1$) A occurs in both sides of the membrane. Each side of the membrane has its own osmotic pressure (with respect to pure solvent)



Flux for RO is then

$$\Phi_{VB} = \frac{P_B}{\delta} [(p_2 - p_1) - (\pi_2 - \pi_1)] = \frac{P_B}{\delta} (\Delta p - \Delta \pi)$$

Φ_{VB} ... volumetric flux [$\text{m}^3 \text{ m}^{-2} \text{ s}^{-1}$]

P_B ... **permeability** of membrane for B

δ ... **thickness**

Osmotic pressure can be calculated from van't Hoff equation:

$$\pi = \beta c_A RT = a c_A$$

Kinetics for UF

A is dispersed in B, typically A is a large molecule $\rightarrow c_A$ is small $\rightarrow \pi$ is small $\rightarrow \Delta\pi \doteq 0$. Therefore

$$\Phi_{VB} = \frac{P_B}{\delta} \Delta p$$

However, in UF a gel layer often forms close to the membrane on the retentate side.

Additional explanation to RO

If the membrane is non-ideal, i.e. partly permeable for A (rejection coefficient < 1) then the flux of A due to diffusion is

$$\Phi_A = J_A = \frac{P_A}{\delta} (M c_{AR} - c_{AP})$$

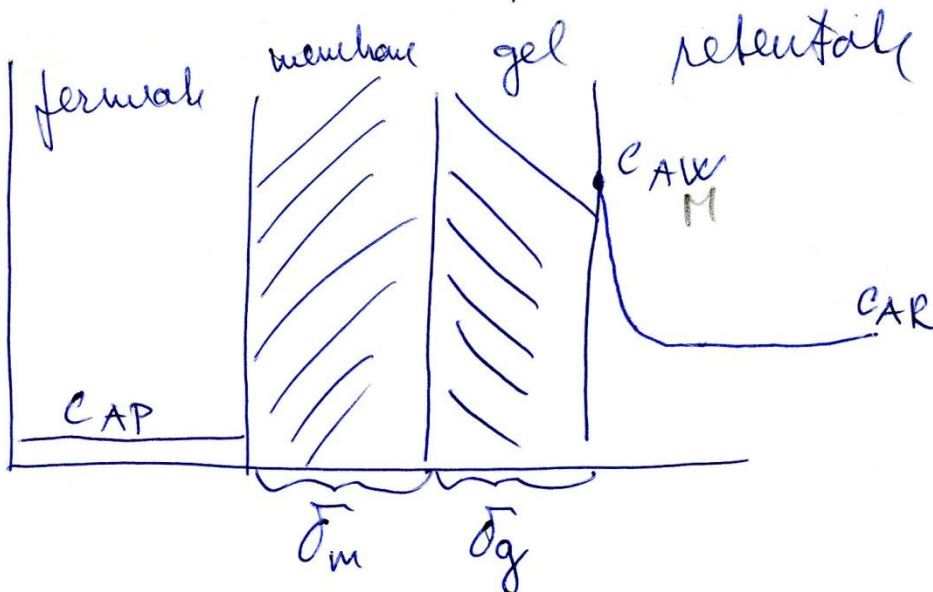
Also from definition

$$\Phi_A = c_{AP} \Phi_V \approx c_{AP} \Phi_{VB}$$

i.e. the total volumetric flux is approximately equal to flux of B. Using expression for Φ_{VB} , Φ_A and definition of $R = 1 - \frac{c_{AP}}{c_{AR}}$ we obtain:

$$R = 1 - \frac{c_{AP}}{c_{AR}} = 1 - \frac{M}{1 + \alpha_{BA}(\Delta p - a(M c_{AR} - c_{AP}))}$$

where M is polarization modulus and $\alpha_{BA} = \frac{P_B}{P_A}$ selectivity, α_{BA} has a unit $[\text{Pa}^{-1}]$ or $[\text{atm}^{-1}]$...



Therefore there are two resistances for the transfer of B through the membrane and the gel (and in addition there can be concentration polarization). Extended flux equation is then

$$\Phi_{VB} = \frac{\Delta p}{\underbrace{\frac{\delta_M}{P_B} + \frac{\delta_g}{P_g}}_{\text{sum of resistances}}}$$

where P_g is the permeability of the gel for B.

Carman-Kozeny equation (hydrodynamic flow through porous material) determines the permeability of the gel:

$$P_g = \frac{d_p^2 \varepsilon^3}{150 \eta (1 - \varepsilon)^2}$$

where

d_p ... diameter of the particles forming the gel

ε ... porosity of the gel = $\frac{\text{volume of free space}}{\text{volume of gel}}$

η ... viscosity of the fluid

Remarks:

- Symbol J_V is also used instead of Φ_V
- Flux is sometimes expressed by explicitly using viscosity η

$$\Phi_{VB} = J_{VB} = \frac{P'_B}{\eta \delta} \Delta p \quad \dots \text{no gel layer}$$

or

$$\Phi_{VB} = J_{VB} = \frac{\Delta p}{\frac{\eta \delta_m}{P_B} + \frac{\eta \delta_g}{P'_g}}$$

where

$$P_B = \frac{P'_B}{\eta} \quad \text{and} \quad P_g = \frac{P'_g}{\eta}$$

SI unit of P_B and P_g is [$\text{m}^2 \text{s}^{-1} \text{Pa}^{-1}$]; unit of P'_B, P'_g is [m^2]

- When a gel is formed J_{VB} is **constant** (balance between convective transport of A toward the membrane and back diffusion). When Δp is suddenly increased J_{VB} instantaneously increases, however, the gel layer thickness δ_g starts growing until the original value of J_{VB} is restored due to increased resistance.
- If the membrane is non-ideal the molar flux of a through the membrane is

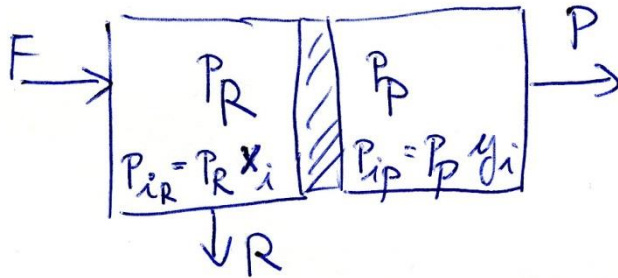
$$J_{nA} = M c_{AR} (1 - R_V) J_{VB}$$

$$R_V = 1 - \frac{c_{AP}}{c_{AR}} \quad \dots \text{apparent rejection coefficient} < 1$$

$$M = \frac{c_{AW}}{c_{AR}} \quad \dots \text{ polarization modulus}$$

Gas permeation

Gases are dissolved in and diffuse through the membrane. Modules with hollow fibers and spiral-wound membranes are used → purification of hydrogen, CO₂, production of N₂ and O₂ from air. Driving force is **partial pressure**.



$$J_{Vi} = \frac{P_i}{\delta_m} (p_{iR} - p_{iP}) = \frac{P_i}{\delta_m} (p_R x_i - p_P y_i)$$

The flux is

$$J_{Vi} = \frac{\dot{V}_{iP}}{A} = \frac{\dot{n}_P y_i}{A \hat{c}_i}$$

\dot{n}_P ... molar flux of permeate

\hat{c}_i ... molar density of pure component i; for ideal gases $\hat{c}_i = \frac{p_i}{RT}$ does not depend on component

for A:

$$\frac{\dot{n}_P y_A}{A \hat{c}_A} = \frac{P_A}{\delta_m} (p_R x_A - p_P y_A)$$

for B:

$$\frac{\dot{n}_P (1 - y_A)}{A \hat{c}_B} = \frac{P_B}{\delta_m} (p_R (1 - x_A) - p_P (1 - y_A))$$

From mass balance:

$$x_A = \frac{x_{AF} - \theta y_A}{1 - \theta}$$

We assume ideal gas, $\hat{c}_A = \hat{c}_B$ and divide first two equations:

$$\frac{y_A}{1 - y_A} = \alpha_{BA} \frac{p_R x_A - p_P y_A}{p_R (1 - x_A) - p_P (1 - y_A)}$$

$$\alpha_{BA} = \frac{P_B}{P_A} \dots \text{selectivity (should be } > 40)$$

By using mass balance we determine y_A :

$$\alpha y_A^2 + b y_A + c = 0$$

$$a = \left(\frac{\theta}{1 - \theta} + \frac{p_P}{p_R} \right) (\alpha_{BA} - 1)$$

$$b = (1 - \alpha_{BA}) \left(\frac{p_P}{p_R} + \frac{\theta}{1 - \theta} + \frac{x_{AF}}{1 - \theta} \right) - \frac{1}{1 - \theta}$$

$$c = \alpha_{BA} \frac{x_{AF}}{1 - \theta}$$

Remark: P_i can be approximately expressed as $P_i = K_i^{-1} D_i = S_i D_i$

K_i	... Henry constant → absorption to membrane
D_i	... diffusivity → diffusion through membrane
$S_i = K_i^{-1}$... solubility

Pervaporation (PV)

Retentate is a liquid. Components diffuse through the membrane and evaporate on the permeate side due to lowered pressure. Membrane is **swollen** in the retentate side and **shrunk** on the permeate side. Also temperature drops across the membrane → complex diffusive process.

PV is used to separate azeotropic mixture obtained in rectification. A simplified description of the transport through the membrane makes use of empirically determined **selectivity** α_{BA} . It is assumed that (analogy to distillation)

$$\alpha_{AB} = \frac{y_A/x_A}{y_B/x_B} = \frac{y_A(1 - x_A)}{x_A(1 - y_A)}$$

Mass balance

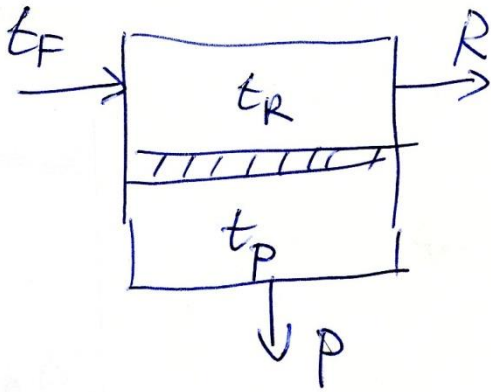
$$x_A = \frac{x_{AF} - \theta y_A}{1 - \theta}$$

by eliminating x_A :

$$(\alpha_{AB} - 1) \theta y_A^2 - [(1 - \theta) + (\alpha_{AB} - 1)x_{AF} + \alpha_{AB}\theta] y_A + \alpha_{AB} x_{AF}$$

Enthalpy balance for PV

Feed is hot, retentate is colder and permeate is coolest due to evaporation. There is no external heat supply or removal. For simplicity we will assume that $t_R = t_P$ (not true but for enthalpy balance is OK)



$$\dot{n}_F c_{pF} (t_F - t_{ref}) = \dot{n}_R c_{pR} (t_R - t_{ref}) + \dot{n}_P (c_{pP} (t_P - t_{ref}) + \Delta h_{vap})$$

where

$$\Delta h_{vap} = y_A \Delta h_{vap,A} + (1 - y_A) \Delta h_{vap,B}$$

and similarly

$$c_{pF} = x_{AF} c_{pA} + (1 - x_{AF}) c_{pB}$$

c_p is evaluated at $\bar{t} = \frac{t_F + t_{ref}}{2}$; c_{pR} and c_{pP} are analogous but not needed

Assuming $t_{ref} = t_P = t_R$

$$\dot{n}_F c_{pF} (t_F - t_{ref}) = \dot{n}_P \Delta h_{vap}$$

Then the cut

$$\theta = \frac{\dot{n}_P}{\dot{n}_F} = \frac{c_{pF} (t_F - t_{ref})}{\Delta h_{vap}}$$