Lecture 12. Transport in Membranes (2)

- Module Flow Patterns
  - Perfect mixing
  - Countercurrent flow
  - Cocurrent flow
  - Crossflow
- Membrane Cascades
- External Mass–Transfer Resistances
- Concentration Polarization and Fouling
• The flow pattern can significantly affect the degree of separation and the membrane area
• For countercurrent and cocurrent flow, permeate fluid at a given location on the downstream side consists of fluid that has just passed through the membrane plus the permeate fluid flowing to that location
• For crossflow, there is no flow of permeate fluid along the membrane
Crossflow Pattern (1)

The pressure ratio, \( r = \frac{P_P}{P_F} \), and the ideal separation factor, \( \alpha_{A,B}^* \), are assumed constant.

At the differential element, local mole fractions in the retentate and permeate are \( x_i \) and \( y_i \).

\( \theta \): cut, fraction of feed permeated \( \left( \frac{n_p}{n_F} \right) \)

Penetrant molar flux: \( \frac{dn}{dA_M} \)

- **Expression for the local permeate composition**

\[
\frac{y_A}{1 - y_A} = \alpha_{A,B}^* \left[ \frac{x_A - ry_A}{(1 - x_A) - r(1 - y_A)} \right]
\]

- **Material balance for A around the differential-volume element**

\[
y_A dn = d(nx_A) = x_A dn + ndx_A
\]

\[
\frac{dn}{n} = \frac{dx_A}{y_A - x_A} = \left[ \frac{1 + (\alpha - 1)x_A}{x_A(\alpha - 1)(1 - x_A)} \right] dx_A
\]

where \( \alpha = \alpha_{A,B}^* \)
Crossflow Pattern (2)

• Integration from the intermediate location of the differential element to the final retentate (from \( n \) to \( n_R \); from \( x_A \) to \( x_{RA} \))

\[
n = n_R \left[ \left( \frac{x_A}{x_{RA}} \right)^\left( \frac{1}{\alpha-1} \right) \left( \frac{1 - x_{RA}}{1 - x_A} \right)^\left( \frac{1}{\alpha-1} \right) \right]
\]

• Mole fraction of A in the final permeate

\[
y_{PA} = \int_{x_{FA}}^{x_{RA}} y_A \, dn/\theta n_F = x_{RA}^{(1-\alpha)} \left( \frac{1 - \theta}{\theta} \right) \left[ (1 - x_{RA})^\left( \frac{\alpha}{\alpha-1} \right) \left( \frac{x_{FA}}{1 - x_{FA}} \right)^\left( \frac{\alpha}{\alpha-1} \right) - x_{RA}^\left(\frac{1-\alpha}{1-\alpha}right) \right]
\]

• Differential rate of mass transfer of A across the membrane

\[
y_A \, dn = \frac{P_{MA}}{l_M} dA_M \left( x_A P_F - y_A P_P \right)
\]

• Total membrane surface area

\[
A_M = \int_{x_{RA}}^{x_{FA}} \frac{l_M y_A \, dn}{P_{MA} (x_A P_F - y_A P_P)}
\]
Cascades (1)

- **Cascades**: aggregates of stages
  - Accomplish separations that cannot be achieved in a single stage
  - Reduce the amounts of separating agent required
  - Make efficient use of raw materials

- Two or more streams are intimately contacted
  - Promote rapid mass and heat transfer
  - The separated phases leaving the stage approach equilibrium
Cascades (2)

- Single section of stages
  - Streams entering and leaving are only from the ends
  - Used to recover components from a feed stream

- Two sections of stages
  - Consist of one section above the feed and one below
  - Used to make a sharp separation between two selected feed components, key components
Membrane Cascades (1)

- Membrane-separation systems often consist of multiple-membrane modules because a single module may not be large enough to handle the required feed rate
  - A number of modules of identical size in parallel with retentates and permeates from each module combined
  - The parallel units function as a single stage
  - In multiple stages, the combined retentate from each stage becomes the feed for the next stage

One stage

Multiple stage
Membrane Cascades (2)

- Single-stage membrane-separation process: a single membrane module or a number of such modules arranged in parallel or in series without recycle
  - The extent to which a feed mixture can be separated is limited and determined by the separation factor, $\alpha$
  - The separation factor depends on module flow patterns, the permeability ratio (ideal separation factor), the cut ($\theta$), and the driving force for membrane mass transfer

- To improve purity and recovery, membrane stages are cascaded with recycle
Membrane Cascades (3)

- Multiple-stage countercurrent recycle cascade

- Permeate is enriched in components of high permeability in an enriching section
- The retentate is enriched in components of low permeability in a stripping section
- For a cascade, additional factors that affect the degree of separation are the number of stages and the recycle ratio (permeate recycle rate/permeate product rate)
Membrane Cascades (4)

- It is best to manipulate the cut and reflux at each stage so as to force compositions of the two streams entering each stage to be identical (ideal).
  - This corresponds to the least amount of entropy production for the cascade and, thus, the highest second-law efficiency.
- In the case of gas permeation, compression costs are high → often limited to just two or three stages.

**Two-stage stripping cascade**
- Designed to obtain a purer retentate

**Two-stage enriching cascade**
- Designed to obtain a purer permeate
Membrane Cascades (5)

Two-stage enriching cascade with additional premembrane stage

- Addition of a premembrane stage may be attractive when
  (1) feed concentration is low in the component to be passed preferentially through the membrane
  (2) desired permeate purity is high
  (3) separation factor is low
  (4) a high recovery of the more permeable component is desired
External Mass–Transfer Resistances (1)

• When mass–transfer resistances external to the membrane are not negligible,
  – Gradients exist in the boundary layers (or films) adjacent to the membrane surfaces
  – Reduces the driving force for mass transfer across the membrane and, therefore, the flux of penetrant

• Gas permeation by solution–diffusion is slow compared to diffusion in gas boundary layers or films
  → external mass–transfer resistances are negligible

• Membrane processes involving liquid (dialysis, reverse osmosis, pervaporation): diffusion in liquid boundary layers and films is slow
  → concentration polarization (accumulation of non–permeable species on the upstream surface of the membrane) cannot be neglected
External Mass–Transfer Resistances (2)

- Mass transfer of liquids with a porous membrane (at steady state)

\[ N_i = k_{i_F} (c_{i_F} - c_{i_0}) = \frac{D_{e_i}}{l_M} (c_{i_0} - c_{i_L}) = k_{i_p} (c_{i_L} - c_{i_p}) \]

\[ N_i = \frac{c_{i_F} - c_{i_p}}{\frac{1}{k_{i_F}} + \frac{l_M}{D_{e_i}} + \frac{1}{k_{i_p}}} \]

- Mass transfer of liquids with a nonporous membrane (at steady state)

\[ N_i = k_{i_F} (c_{i_F} - c'_{i_0}) = \frac{K_i D_i}{l_M} (c'_{i_0} - c'_{i_L}) = k_{i_p} (c'_{i_L} - c_{i_p}) \]

\[ N_i = \frac{c_{i_F} - c_{i_p}}{\frac{1}{k_{i_F}} \frac{1}{K_i D_i} + \frac{1}{k_{i_p}}} \]

\( k_{iF} \) & \( k_{ip} \): mass–transfer coefficients
External Mass–Transfer Resistances (3)

- Resistances to mass flux: \( \frac{1}{k_{i_F}}, \frac{l_M}{D_{e_i}} (\text{or} \frac{l_M}{K_i D_i}), \frac{1}{k_{i_P}} \)

- Mass transfer coefficients depend on fluid properties, flow–channel geometry, and flow regime

- Membrane resistances \( \frac{l_M}{D_{e_i}} \) and \( \frac{l_M}{K_i D_i} \) can be replaced by \( \frac{l_M}{P_{M_i}} \) or \( \frac{1}{P_{M_i}} \)

- The empirical film–model correlation of mass–transfer coefficients for channel flow

\[
N_{Sh} = k_i d_H / D_i = a N_{Re}^b N_{Sc}^{0.33} (d_H / L)^d
\]

\[
N_{Re} = d_H v \rho / \mu \\
N_{Sc} = \mu / \rho D_i \\
d_H: \text{hydraulic diameter} \\
v: \text{velocity}
\]
Concentration Polarization and Fouling (1)

- Concentration polarization occurs in membrane separators when the membrane is permeable to A, but relatively impermeable to B.
- Molecules of B are carried by bulk flow to the upstream surface of the membrane, where they accumulate, causing their concentration at the surface of the membrane to increase in a polarization layer.
- The equilibrium concentration of B in this layer is reached when its back-diffusion to the bulk fluid on the feed-retentate side equals its bulk flow toward the membrane.
Concentration Polarization and Fouling (2)

- Concentration polarization is most common in pressure-driven membrane separations involving liquids, such as reverse osmosis and ultrafiltration, where it reduces the flux of A.
  - The polarization effect can be serious if the concentration of B reaches its solubility limit on the membrane surface.
  → A precipitate of gel may form, the result being fouling on the membrane surface or within membrane pores, with a further reduction in the flux of A.

- The most straightforward way of minimizing concentration polarization is to reduce the film thickness by increasing turbulent mixing at the membrane surface.