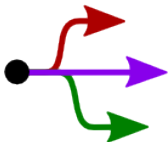


Separation Processes

ChE 4M3



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kevin.dunn@mcmaster.ca
<http://learnche.mcmaster.ca/4M3>

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Membranes

On a loose sheet of paper, please list/describe 5 topics related to membranes that you want to learn about in the next 5 classes.

For example:

- ▶ the equations to model fluid flow through a membrane
- ▶
- ▶
- ▶
- ▶
- ▶

e.g. recall interesting ideas from Henk Koops' talk; check the internet; talk with the person next to you

Introduction to membranes

Please refer to Henk Koops' slides/video from 28 September 2012
on [the course website](#)

Why use membranes?

Some really difficult separations:

- ▶ finely dispersed solids; density close to liquid phase; gelatinous particles
- ▶ dissolved salts
- ▶ non-volatile organics (e.g. **humic substances**)
- ▶ biological materials: sensitive to the environment
 - ▶ cannot centrifuge
 - ▶ cannot sediment

It is usually worth asking:

How does nature separate?

- ▶ energy efficient
- ▶ effective
- ▶ maybe slow?

Why use membranes?

Relatively new separation step (“new” meaning since 1960 to 1980s)

- ▶ often saves energy costs over alternative separations
 - ▶ ambient temperature operation
- ▶ often easier to operate and control



Modules:

- ▶ feed stream split into parallel units
- ▶ easier to maintain and replace parts
- ▶ can be expanded as needs grow

Challenges in membrane design

Challenges:

- ▶ withstanding high pressure differences but still have thin membrane
- ▶ dealing with fouling and cleaning
- ▶ increasing selectivity (separation factor) for specific application areas
- ▶ uniformity of pore sizes
- ▶ temperature stability (e.g. steam sterilization)

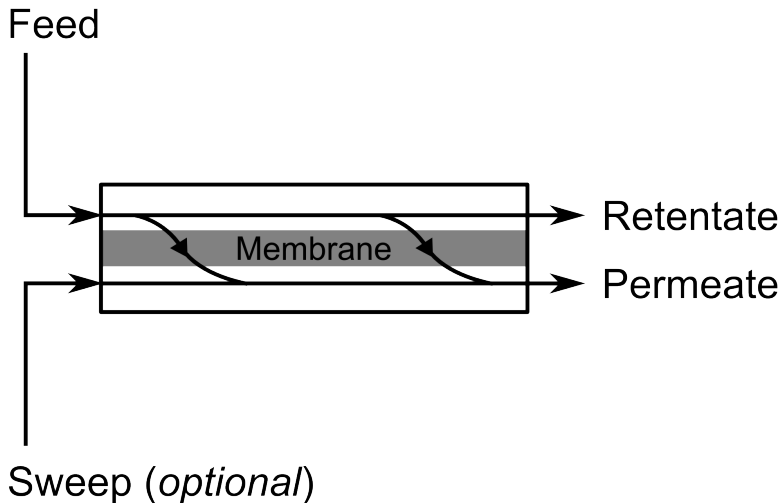
Market size

TABLE 20-16 Membrane Market in 2005

Segment	\$M/yr Size	Applications	Characteristics
Dialysis	~2,000	Medical	Mature growing 5%
Reverse osmosis	~500	Water treatment	Growing 10%
Microfiltration	~500	Water, food, pharm.	Growing 10%
Ultrafiltration	~400	Water, food, pharm.	
Gas separation	~500	Nitrogen	Nascent
Electrodialysis	~100	Water	
Pervaporation	~5	Solvent/water	
Facilitated transport	0	None	In development

[Perry's: Chapter 20, 8ed]

Let's formalize some terminology



More terminology

semipermeable: partially permeable, e.g. your skin allows certain size particles in, but not others

mass separating agent: the membrane itself

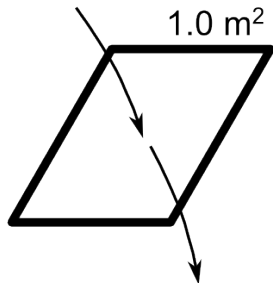
energy separating agent: the applied pressure (pressure drop)

$$\text{porosity} = \frac{\text{area of open pores}}{\text{total surface area}}$$

What is flux?

The (volumetric) or (molar) or (mass) flow per unit time for 1 unit of area

- ▶ $J = \text{flux} = \frac{\text{transfer rate}}{\text{transfer area}}$
- ▶ e.g. $42 \text{ mol.s}^{-1}.\text{m}^{-2}$
- ▶ never simplify the units: write $13 \text{ m}^3.\text{s}^{-1}.\text{m}^{-2}$
- ▶ **do not write** 13 m.s^{-1}



General principle

For a given unit area, we want the highest flux possible (at the lowest possible cost)

Membrane classification

Table 8.1. Classification of membrane separation processes for liquid systems

Name of process	Driving force	Separation size range	Examples of materials separated
Microfiltration	Pressure gradient	10–0.1 μm	Small particles, large colloids, microbial cells
Ultrafiltration	Pressure gradient	<0.1 μm –5 nm	Emulsions, colloids, macromolecules, proteins
Nanofiltration	Pressure gradient	~ 1 nm	Dissolved salts, organics
Reverse osmosis (hyperfiltration)	Pressure gradient	<1 nm	Dissolved salts, small organics
Electrodialysis	Electric field gradient	<5 nm	Dissolved salts
Dialysis	Concentration gradient	<5 nm	Treatment of renal failure

[Richardson and Harker, p 438]

Transport through a membrane

Why study theoretical models?

All forms of membrane applications rely to some extent on the same equation **structure**. The details will change.

Will allow us to:

- ▶ troubleshoot problems with the process
- ▶ predict expected impact of improvements/changes to the process
- ▶ used for crudely sizing the unit (order of magnitude estimates)

Examples you will be able to solve

1. how long should we operate unit at constant ΔP to achieve desired separation?
2. what is the mass transfer coefficient through the lab membrane?
3. what pressure drop (and therefore pump size) do I expect?
4. how many cassettes does this application require?

The general equation

$$\frac{\text{transfer rate}}{\text{transfer area}} = \text{flux} = \frac{(\text{permeability})(\text{driving force})}{\text{thickness}} = \frac{\text{driving force}}{\text{resistance}}$$

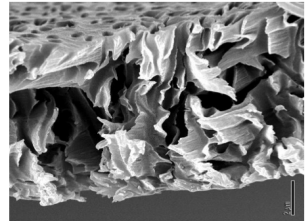
Symbolically:

$$\rho_f \frac{Q_p}{A} = \frac{\rho_f}{A} \cdot \frac{dV}{dt} = J = \frac{(\text{permeability})(\text{driving force})}{L} = \frac{\text{driving force}}{R}$$

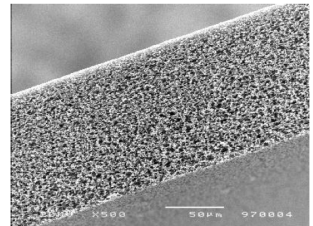
- ▶ permeance = $\frac{\text{permeability}}{L} = \frac{1}{\text{resistance}} = \frac{1}{R} = \text{"mass transfer coeff"}$
- ▶ permeance: easier to measure
- ▶ permeance units: depend on choice of (driving force) and J
- ▶ resistance = $f(\text{thickness, viscosity, porosity, pore size})$
- ▶ we will specifically define resistance in each case

Microfiltration

- ▶ 0.1 μm to 10 μm retained mainly by sieving mechanism
- ▶ conventional filters: not effective below $\sim 5 \mu\text{m}$
- ▶ microfiltration membranes: generally symmetric pores
- ▶ polysulfone membrane
- ▶ porosity as high as $\epsilon = 0.8$
- ▶ driving force = ΔP : 100 to 500 kPa
- ▶ high fluxes at low TMP (trans-membrane pressure)
- ▶ application areas:
 - ▶ yeast cells harvesting
 - ▶ wine/beer/juice clarification
 - ▶ bacteria and virus removal
 - ▶ air filtration
 - ▶ cytology: concentrate up cells



symmetric open structure

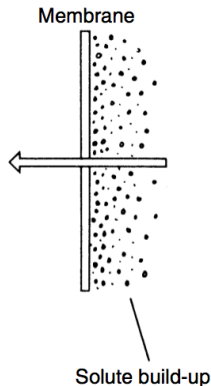


symmetric spongy structure

General modelling equation applied

$$\frac{\rho_f}{A} \cdot \frac{dV}{dt} = \text{Flux} = J = \frac{\Delta P}{\mu (R_m \ell_M + R_c L_c)} \quad \text{Permeate} \leftarrow$$

$$\frac{\rho_f}{A} \cdot \frac{dV}{dt} = \text{Flux} = J = \frac{\Delta P}{\mu (R'_m + R'_c)}$$



J [kg.s⁻¹.m⁻²]

permeate flux

μ [kg.m⁻¹.s⁻¹]

permeate viscosity

ΔP [Pa] = [kg.m⁻¹.s⁻²]

TMP varies for different applications

R_m [m.kg⁻¹]

resistance through membrane (small)

R_c [m.kg⁻¹]

resistance through cake (large)

ℓ_m [m]

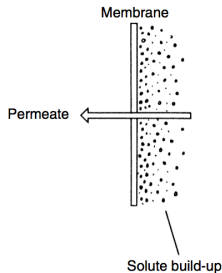
membrane thickness

L_c [m]

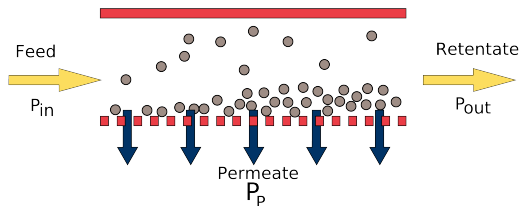
effective cake thickness

Flow patterns for microfiltration

Dead-end flow



Cross-flow (TFF)



- ▶ only for very low concentration feeds
- ▶ else becomes rapidly clogged
- ▶ air filtration and virus removal applications

- ▶ TFF = tangential flow filtration
- ▶ main purpose?

▶ microfiltration tends to have cake build up

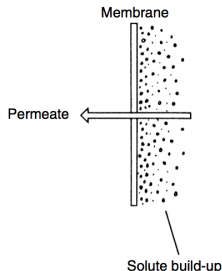
▶ cross-flow induces shearing to erode cake

▶ reduces cake resistance, R'_c

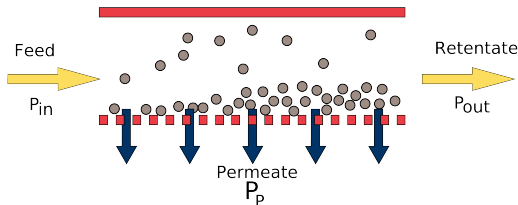
▶ $\Delta P = P_{in} - P_{out} - P_p$

Flow patterns for microfiltration

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 - ▶ microfiltration: tends to have cake build up
 - ▶ cross-flow induces shearing to erode cake
 - ▶ reduces cake resistance, R'_c
 - ▶
$$\Delta P = \frac{P_{in} - P_{out}}{2} - P_p$$

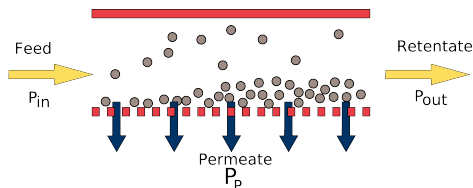
Dead-end flow vs cross-flow geometries

Dead-end flow

- ▶ cake thickness increases with time: $L_c(t)$
- ▶ implies cake resistance changes with time: $R'_c(t)$
- ▶ so for a constant ΔP , implies $J(t)$ falls off

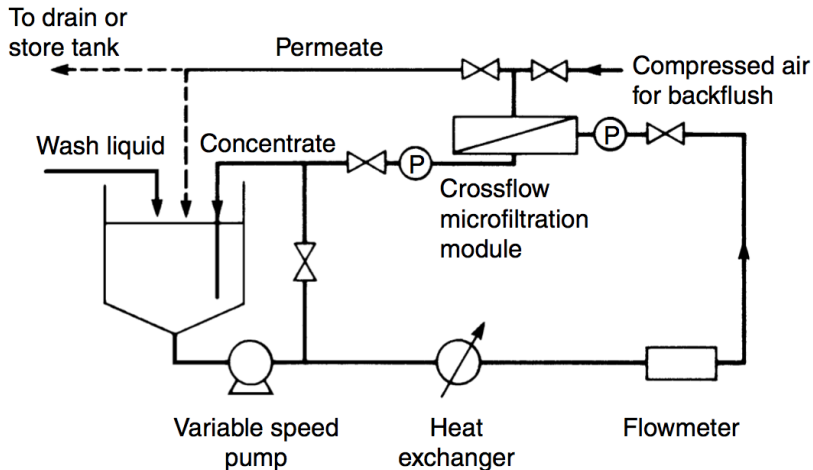
$$J = \frac{\Delta P}{\mu (R'_m + R_c L_c)}$$

Cross-flow (TFF)



- ▶ fluid velocity: 1 to 8 m.s⁻¹ tangentially
- ▶ keeps mass transfer resistance low
- ▶ for a given ΔP : TFF allows us to obtain higher fluxes than dead-end (usually ΔP is 100 to 500 kPa)
- ▶ cannot take lab test results with a filter cloth dead-end and apply it to cross-flow situation

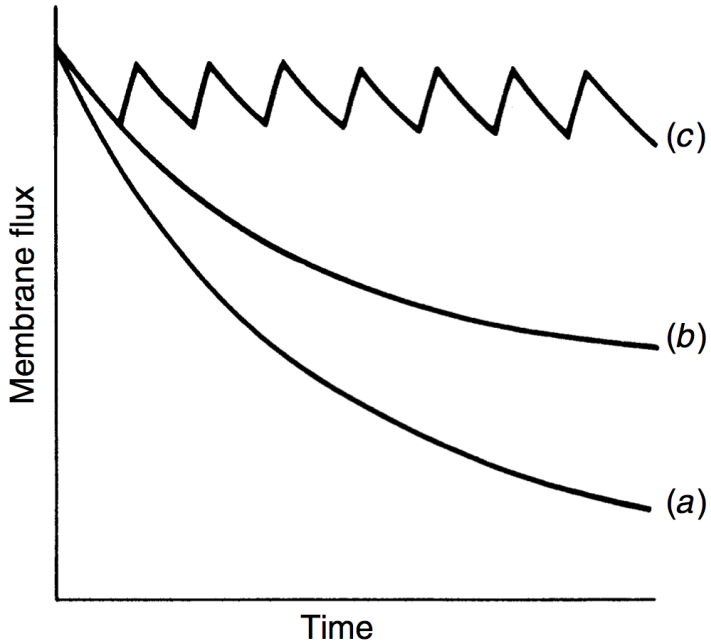
Cross-flow flowsheet



How to pressurize the unit?

1. Supply feed at pressure; valve at retentate to adjust/control ΔP
2. Draw a vacuum at permeate and pull material through membrane

Dealing with fouling



A preliminary design

Main aim

Determine the **size** of a membrane for a required **flow rate** of permeate.

We have a reasonable budget to purchase equipment, and membrane samples from suppliers.

How would you set up your lab experiment(s) to get the information required?

$$J = \frac{Q_p}{A} = \frac{\Delta P}{\mu(R_m L_m + R_c L_c)} = \frac{\Delta P}{\mu(R'_m + R'_c)}$$

- R'_m : estimated using pure solvent through membrane at ΔP
- $R'_c = R_c L_c$: obtained from a plot of J_i vs ΔP_i
 - set different ΔP_i ; then measure corresponding J_i once steady
 - find J_i (interpolate) that gives required Q_p by varying A

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Factors to improve flux

- ▶ increase pressure difference
- ▶ regular backflush
- ▶ choose alternative membrane structure
- ▶ feed concentration kept low
- ▶ shear rate (velocity in cross-flow): reduces $R'_c = R_c L_c$
- ▶ increase temperature of feed
- ▶ nature of the solids deposited: affects resistance R_c

Estimating the cake resistance, R_c

- ▶ $R'_{c,v} = R_{c,v} L_c = R_{c,v} \frac{V_{\text{cake}}}{A_{\text{membrane}}}$
- ▶ $R_{c,v} = R_c \cdot \rho_f$ and similarly $R_{m,v} = R_m \cdot \rho_f$
- ▶ **Important note:** $R'_{c,v}$ emphasizes that this is a resistance only when $J_v = \frac{J}{\rho_f}$, which has units $[(\text{m}^3 \cdot \text{s}^{-1}) \cdot \text{m}^{-2}]$
- ▶ Carman relationship: $R_{c,v} = 180 \left(\frac{1-e}{e^3} \right) \left(\frac{1}{D_p^2} \right)$
- ▶ e = porosity of the cake; $e \sim 0.4$ if unknown
- ▶ D_p = Sauter mean particle diameter [m]
- ▶ L_c = estimated cake thickness [m]
- ▶ $R'_{c,v}$ has units of $[\text{m}^{-1}]$
- ▶ $R_{c,v}$ has units of $[\text{m}^{-2}]$

Microfiltration example

The previous lab experiment to determine mass-transfer resistance is preferred. But we can estimate it.

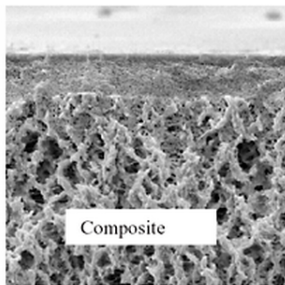
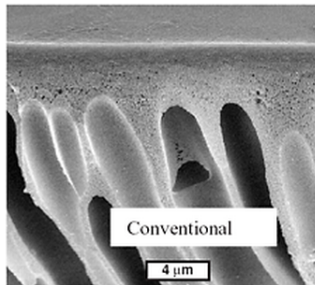
Water microfiltration

- ▶ Constant $\Delta P = 50\text{kPa}$ applied in cross-flow membrane set up
- ▶ Membrane area $= 50\text{cm}^2 = 0.005\text{m}^2$
- ▶ Pure water at this ΔP produced a flux of $1.0\text{ kg}\cdot\text{s}^{-1}\cdot\text{m}^{-2}$
- ▶ Feed at this same TMP produced a flux of $0.065\text{ kg}\cdot\text{s}^{-1}\cdot\text{m}^{-2}$ permeate
- ▶ What is the estimated thickness of the cake build-up if the average particle size diameter is $2\mu\text{m}$?

Practical use of this example?

Ultrafiltration (UF)

- ▶ 5 nm to 100 nm ($0.1\ \mu\text{m}$) particles are retained
- ▶ 1 to 1000 kDa particles are retained (move to using molecular weight)
 - ▶ 1 dalton = 1 atomic mass unit
 - ▶ 1 kilodalton = 1000 dalton = 1000 g/mol
 - ▶ particles with lower molecular weight, e.g. most solvents, pass through
- ▶ pore sizes: 1 to 20nm
- ▶ typical fluxes:
 $J_v = 0.01\text{ to }0.5\ \text{m}^3\cdot\text{m}^{-2}\cdot\text{hr}^{-1}$
 $J_v = 10\text{ to }50\ \text{L}\cdot\text{m}^{-2}\cdot\text{hr}^{-1}$ (LMH)
- ▶ asymmetric structure
- ▶ almost always operated in TFF



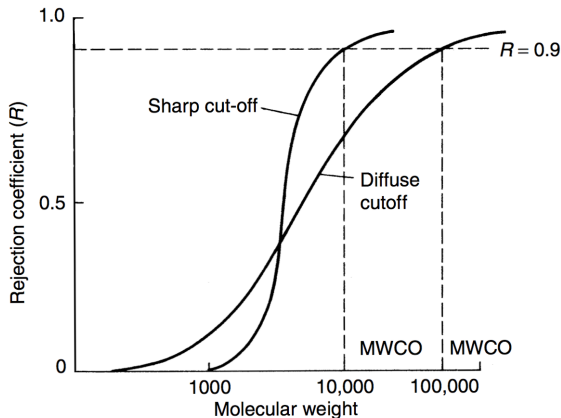
Ultrafiltration applications

UF: loosely considered: “cross-flow filtration at molecular level”

- ▶ Recovery of proteins and high molecular weight materials (solute)
- ▶ Permanent emulsions: e.g. oil phase will not pass
- ▶ Fine colloidal particles: e.g. paint/dyes
- ▶ Large molecules of interest might remain in retentate; permeate discarded
- ▶ e.g. albumin (egg white) concentration
- ▶ e.g. whey processing:
 - ▶ UF first, followed by reverse osmosis (RO)
 - ▶ valuable proteins retained by UF
 - ▶ permeate sent to RO to concentrate smaller molecule sugars and salts
 - ▶ this concentrated permeate: used for ethanol and lactic acid production

Ultrafiltration (UF)

- ▶ driving force = ΔP : 0.1 to 1.0 MPa
- ▶ “tight”, low-permeability side faces the TFF to retain particles
- ▶ this skin layer is about $10\mu\text{m}$ thick; provides selectivity
- ▶ open, high-permeability side mainly for mechanical strength



$$R = 1 - \frac{C_{\text{permeate}}}{C_{\text{feed}}}$$

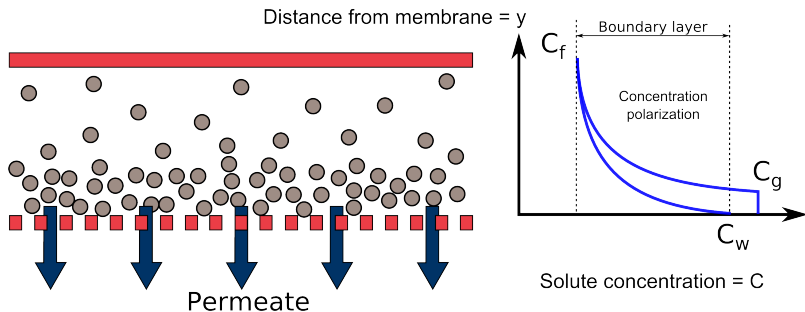
$$R = 1 - \frac{C_p}{C_f}$$

MWCO: molecular weight where $R = 0.9$

i.e. 10% of that molecular weight passes through to the permeate

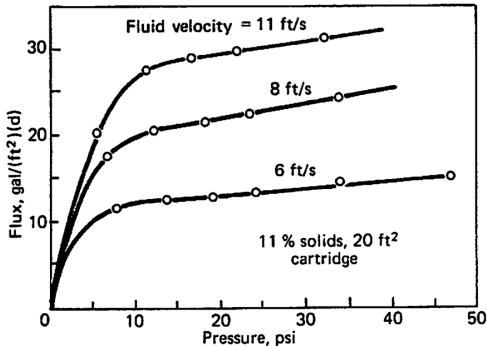
Transport phenomena in UF

- ▶ solute (i.e. particles) carried towards membrane by solvent
- ▶ $J = \frac{\Delta P}{R_m + R_{cp}}$
- ▶ R_m = membrane resistance [m.s^{-1} if J is mass flux]
- ▶ R_{cp} = resistance due to “concentration polarization”
- ▶ R_{cp} effectively is the resistance due to solute boundary layer
- ▶ Mass concentration C_f (feed), steadily increasing to C_w (wall)



Transport phenomena in UF

- ▶ Experimental evidence agrees well with theory ... to a point.
- ▶ Increasing ΔP leads to compacting this layer, increasing C_w
- ▶ So diminishing returns from increasing ΔP
- ▶ Also, there is a strong concentration gradient
- ▶ Diffusion away from membrane due to concentration gradients
- ▶ Eventually solute forms a colloidal gel on the membrane, C_g
- ▶ Adjusting pressure has little/no effect anymore



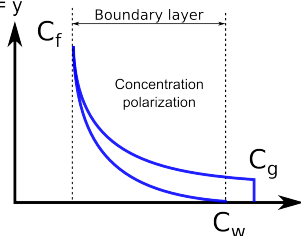
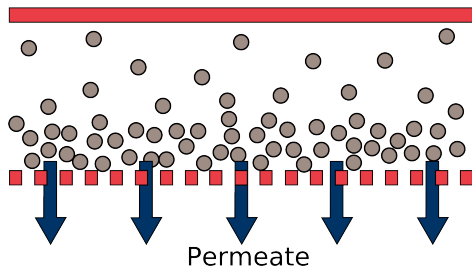
Transport phenomena in UF

- ▶ Mass flow towards membrane: $\frac{J \cdot C}{\rho_f} = J_v C$
- ▶ Diffusion away from membrane: $-D_{AB} \frac{dC}{dy}$

$$-\frac{J}{D_{AB}} \int_0^{L_c} dy = \int_{C_w}^{C_f} \frac{dC}{C}$$

$$\ln \left(\frac{C_w}{C_f} \right) = \frac{J L_c}{D_{AB}} = \frac{J}{h_w}$$

Distance from membrane = y



Solute concentration = C

References

- ▶ Wankat, "Separation Process Engineering", 2nd edition, chapter 16
- ▶ Schweitzer, "Handbook of Separation Techniques for Chemical Engineers", Chapter 2.1
- ▶ Seader, Henly and Roper, "Separation Process Principles", 3rd edition, chapter 14
- ▶ Richardson and Harker, "Chemical Engineering, Volume 2", 5th edition, chapter 8
- ▶ Geankoplis, "Transport Processes and Separation Process Principles", 4th edition, chapter 7 (theory) and chapter 13
- ▶ Ghosh, "Principles of Bioseparation Engineering", chapter 11