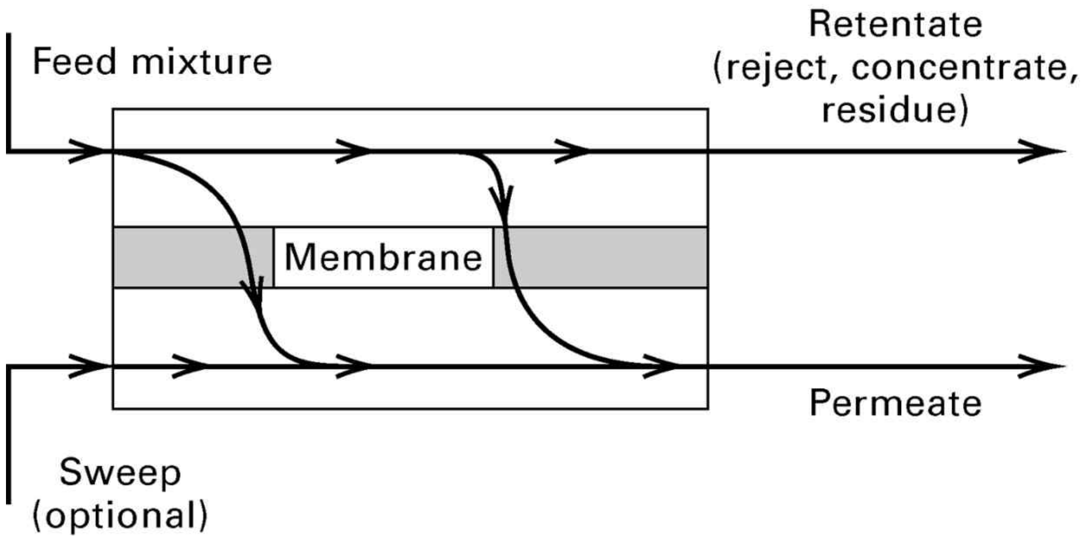
Lecture 10.
Membrane Separation – Materials and Modules

- Membrane Separation
- Types of Membrane
- Membrane Separation Operations
  - Microporous membrane
  - Dense membrane
- Membrane Materials
- Asymmetric Polymer Membrane
- Membrane Modules

Membrane Separation

- Separation by means of a semipermeable barrier (membrane) through which one or more species move faster than another or other species; rate-controlled separation



- Characteristics
  - The two products are usually miscible
  - The separating agent is a semipermeable barrier
  - A sharp separation is often difficult to achieve

History of Membrane Separation

- Large-scale applications have only appeared in the past 60 years
  - 1940s: separation of $^{235}UF_6$ from $^{238}UF_6$ (porous fluorocarbons)
  - 1960s: reverse osmosis for seawater desalinization (cellulose acetate), commercial ultrafiltration membranes
  - 1979: hollow-fiber membrane for gas separation (polysulfone)
  - 1980s: commercialization of alcohol dehydration by pervaporation

- Replacement of more-common separations with membrane
  - Potential: save large amounts of energy
  - Requirements
    - production of high-mass-transfer-flux, defect-free, long-life membranes on a large scale
    - fabrication of the membrane into compact, economical modules of high surface area

Characteristics of Membrane Separation

- Distillation *vs*. gas permeation

  : energy of separation for distillation is usually heat, but for gas permeation is the shaft work of gas compression

- Emerging (new) unit operation

  : important progress is still being made for efficient membrane materials and packaging

- Membrane separator *vs*. other separation equipment
  - More compact, less capital intensive, and more easily operated, controlled, and maintained
  - Usually modular in construction: many parallel units required for large-scale applications

- Desirable characteristics of membrane

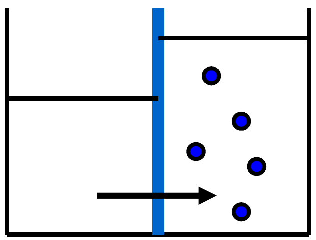
  (1) good permeability, (2) high selectivity, (3) chemical and mechanical compatibility, (4) stability, freedom from fouling, and useful life, (5) amenability, (6) ability to withstand large pressure differences

Types of Membrane

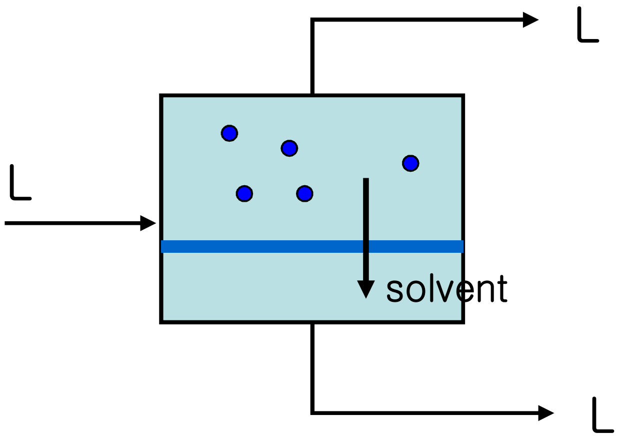
- Microporous membrane
  - Contains interconnected pores of 0.001–10 μm in diameter
  - For small molecules, permeability for microporous membranes is high but selectivity is low
  - Separation based on different diffusion rates through pores
    - Microfiltration (MF): pore sizes of 200–100,000 Å, used to filter bacteria and yeast
    - Ultrafiltration (UF): pore sizes of 10–200 Å, used to separate low-molecular-weight solutes such as enzymes
    - Nanofiltration (NF): pore sizes of 1–10 Å, used in osmosis and pervaporation processes to purity liquids
- Dense membrane (nonporous membrane)
  - Pores, if any, less than a few Angstroms in diameter
  - Diffusing species must dissolve into the polymer and then diffuse through the polymer
  - Separation based on differences in both solubility in the membrane and diffusion rate through the membrane

Membrane Separation Operations (1)

- Osmosis
  Nonporous membrane
  Concentration gradient

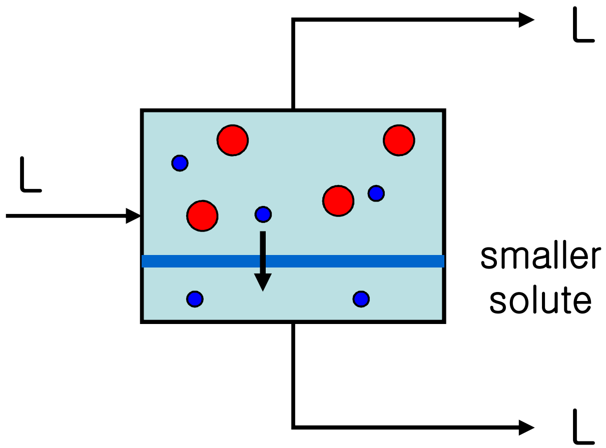


- Reverse osmosis
  Nonporous membrane
  Pressure gradient



Desalination of sea water

- Dialysis
  Porous membrane
  Concentration gradient,
  Pressure gradient



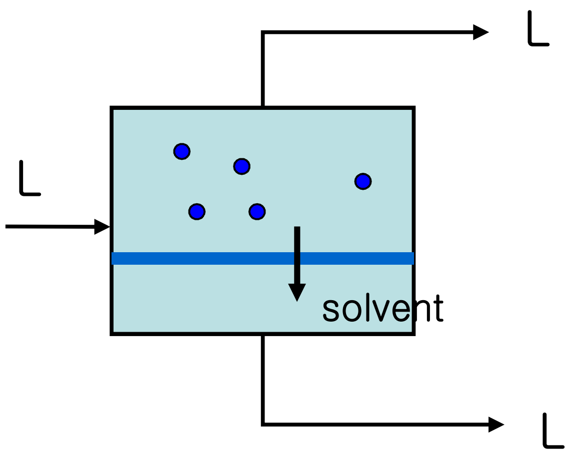
Recovery of caustic from hemicellulose

Membrane Separation Operations (2)

- Microfiltration

Microporous membrane

Pressure gradient



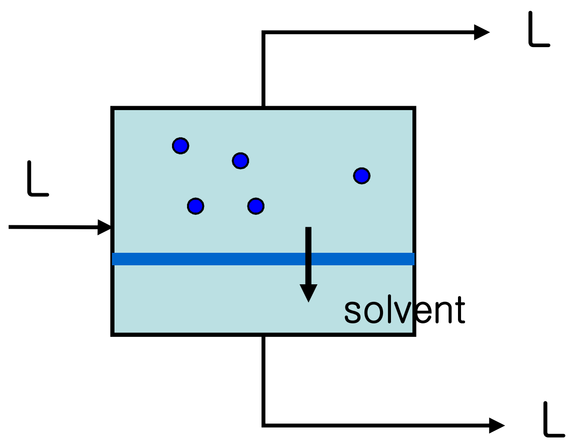
Removal of bacterial from drinking water

(retention of molecules : 0.02 – 10 μm)

- Ultrafilration

Microporous membrane

Pressure gradient



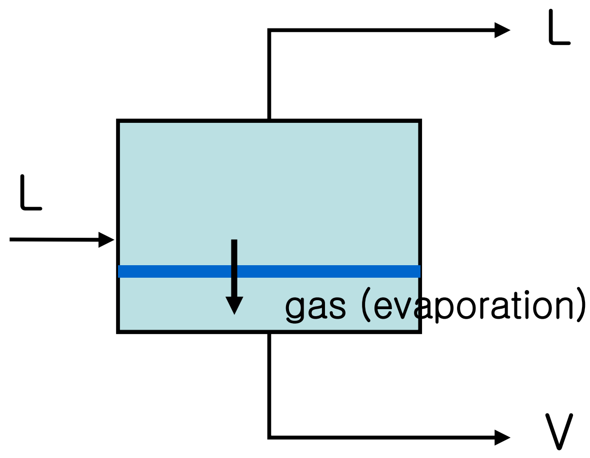
Separation of whey from cheese

(retention of molecules : 1 – 20 nm)

- Pervaporation

Nonporous membrane

Pressure gradient



Separation of azeotropic mixtures

Membrane Separation Operations (3)

- Gas permeation

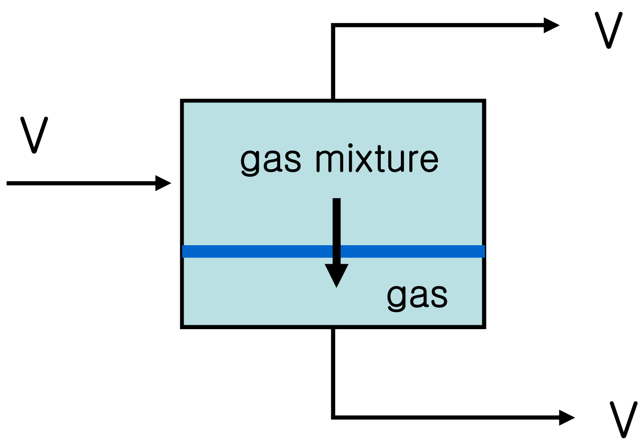
Nonporous membrane

Pressure gradient

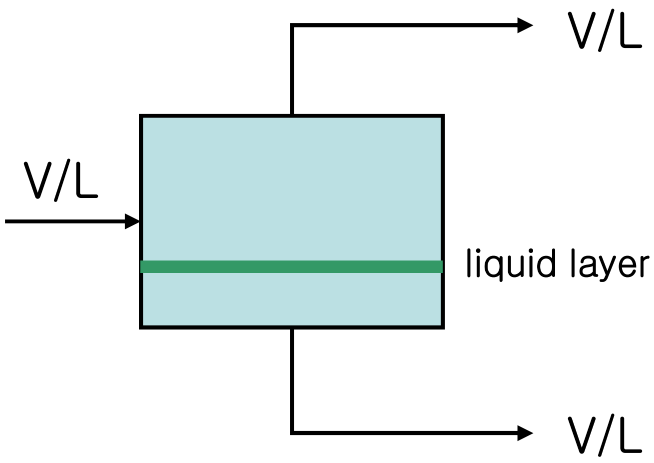
- Liquid membrane

Liquid membrane

Pressure gradient



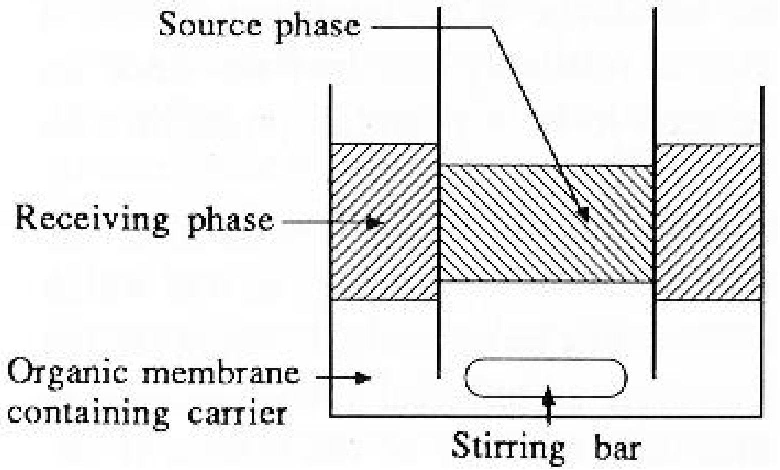
Hydrogen enrichment



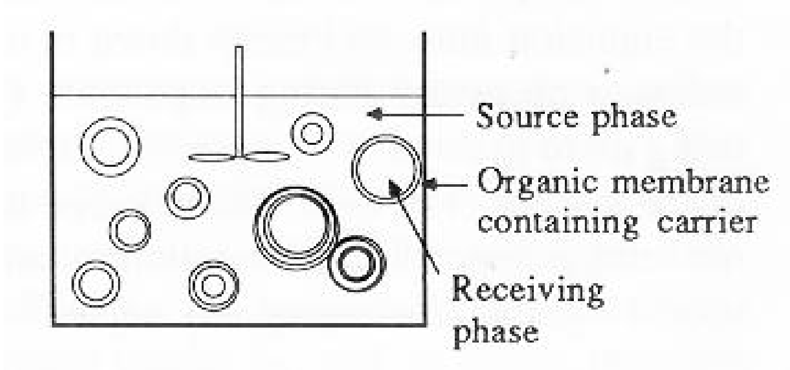
Removal of hydrogen sulfide

Liquid Membrane Types

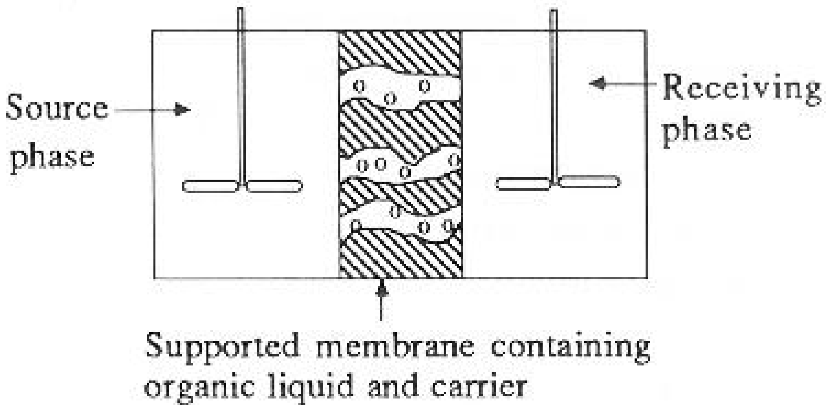
Bulk liquid membrane



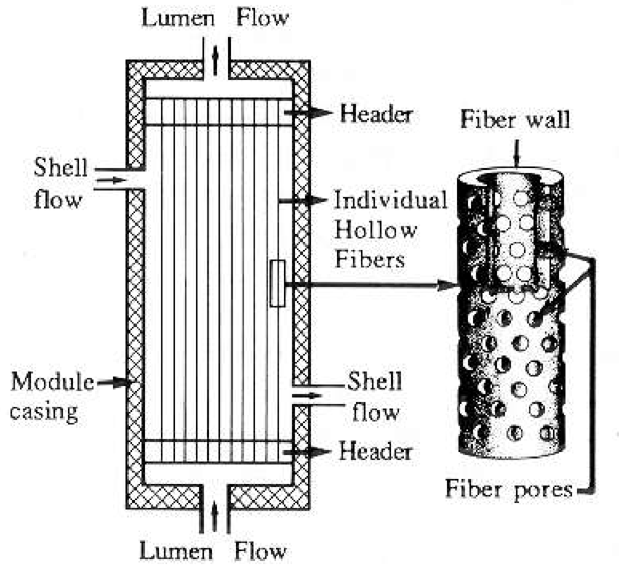
Emulsion liquid membrane



Thin sheet supported liquid membrane



Hollow fiber supported liquid membrane



Membrane Materials (1)

- Typical membrane materials
  - Natural polymers: wool, rubber, and cellulose
  - Synthetic polymers
  - Inorganic materials: microporous ceramics, metals, and carbons

  – Originally processed natural polymers such as cellulose and rubber → synthetic polymers (wide variety of materials have been developed and commercialized since 1930)

  – Almost all industrial membrane materials are made from polymers

- Classification of polymers
  - Thermoplastic polymer: the linear-chain polymers that soften with an increase in temperature and are soluble in organic solvents
  - Thermosetting polymer: highly cross-linked polymers that decompose at high temperature and are not soluble in organic solvents

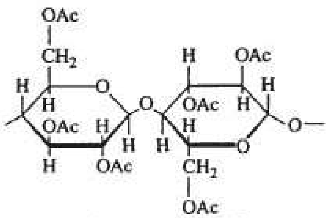
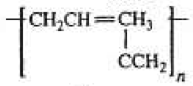
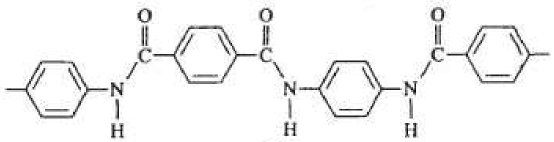
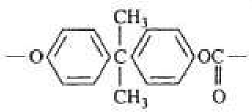
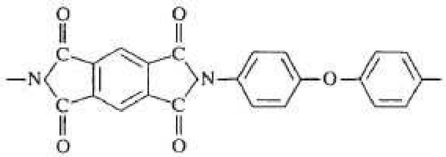
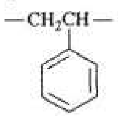
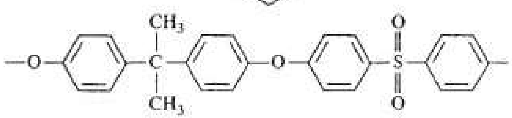
  - Amorphous polymer: glassy in appearance and lacks crystalline structure
  - Crystalline polymer: opaque and has a crystalline structure

Membrane Materials (2)

- Transition temperatures in polymers
  - Glass-transition temperature, T_g: the temperature where a glassy polymer becomes rubbery
  - Melting temperature, T_m: the temperature where a crystalline polymer becomes a melt
  - Most polymers have both amorphous and crystalline regions: degree of crystallinity varying from 5 to 90%
  - Membranes made of glassy polymers can operate below or above T_g; membranes of crystalline polymers must operate below T_m
- Membrane for high temperatures operation
  - Polymer membranes limited to temperatures below 200℃ and chemically inert mixture
  - Operation at high temperatures and with chemically active mixtures requires membranes made of inorganic materials
    - Microporous ceramics, metals, and carbon
    - Dense metal, such as palladium, that allow the selective diffusion of small molecules such as hydrogen and helium

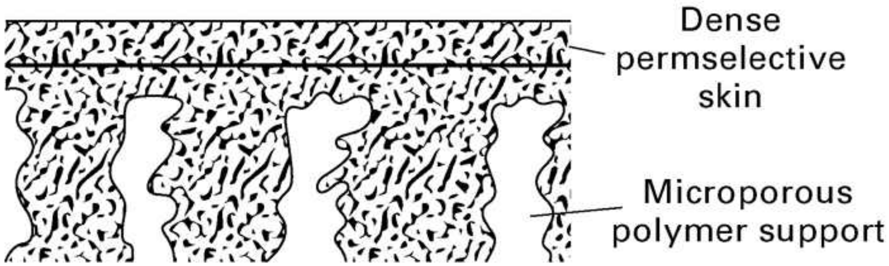
Membrane Materials (3)

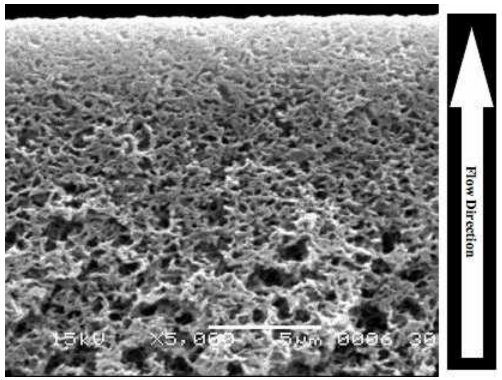
- Common polymers used in membranes

Polymer	Type	Representative Repeat Unit	Glass Transition Temp., °C	Melting Temp., °C
Cellulose triacetate	Crystalline			300
Polyisoprene (natural rubber)	Rubbery		−70	
Aromatic polyamide	Crystalline			275
Polycarbonate	Glassy		150	
Polyimide	Glassy		310–365	
Polystyrene	Glassy		74–110	
Polysulfone	Glassy		190	
Polytetrafluoroethylene (Teflon)	Crystalline	$-CF_2-CF_2-$		327

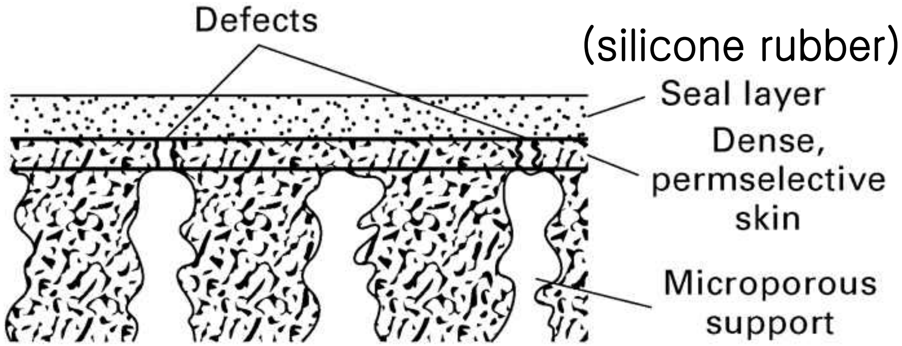
Asymmetric Polymer Membrane

- Asymmetric membrane
  - Solution to the problem that membrane should be thin enough to have high flux while at the same time it should be mechanically strong
  - Thin dense skin (permselective layer) about 0.1–1.0 μm in thick formed over a much thicker microporous layer (support)

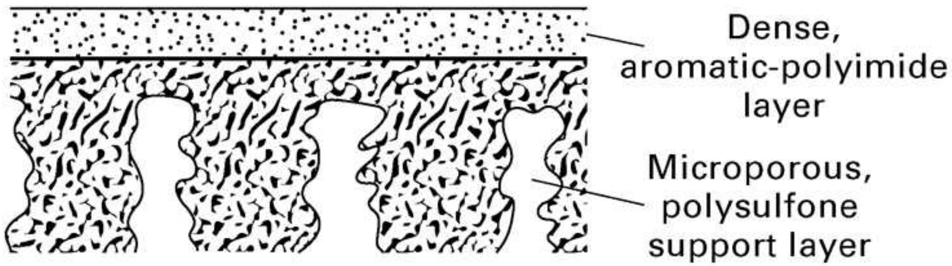




- Caulked membrane

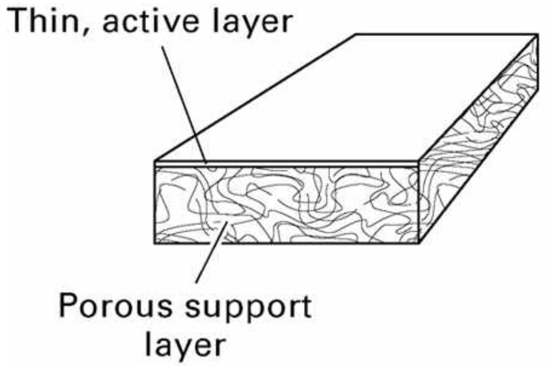


- Thin-film composite

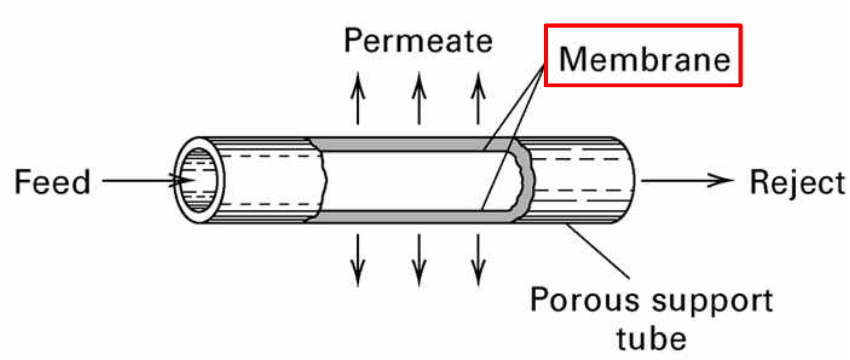


Membrane Modules (1)

- Common membrane shapes

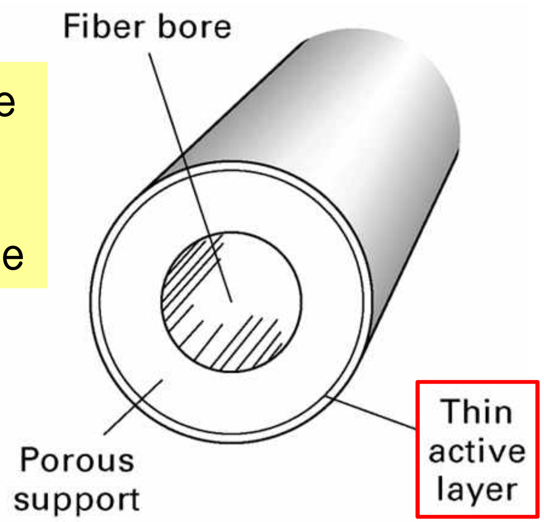


Flat asymmetric or thin-film composite

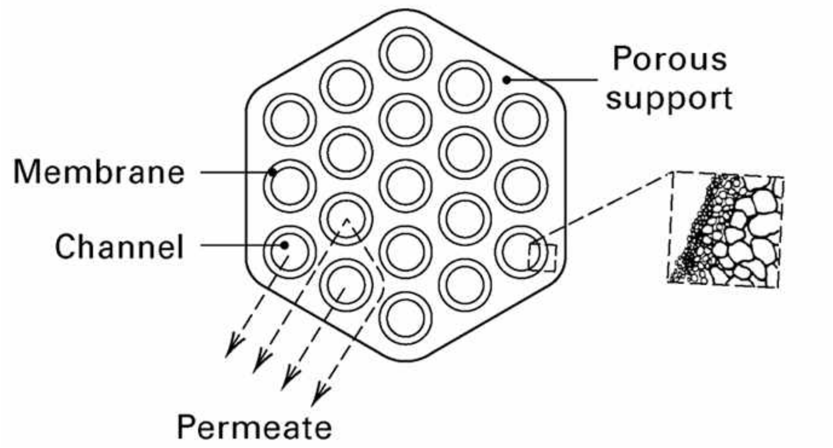


Tubular

Provide a large membrane surface area per unit volume



Hollow fiber

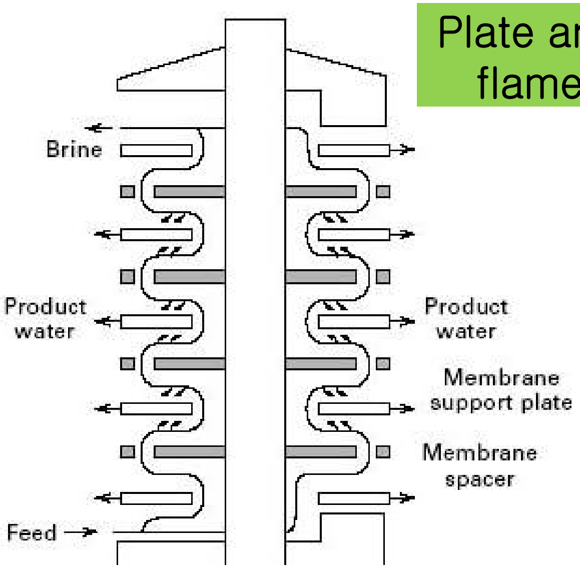


Monolithic

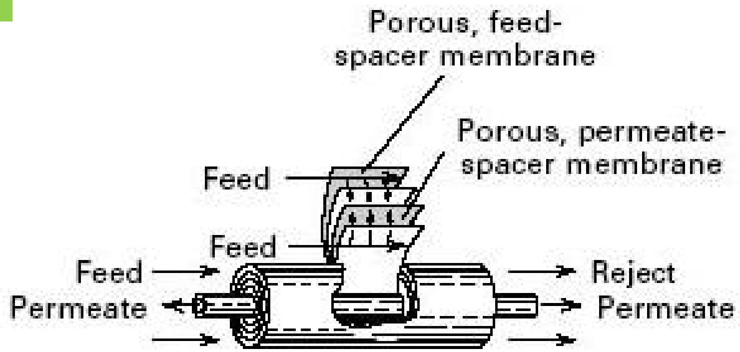
Membrane Modules (2)

- Common membrane modules

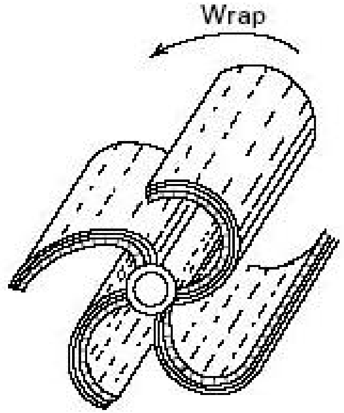
Plate and flame



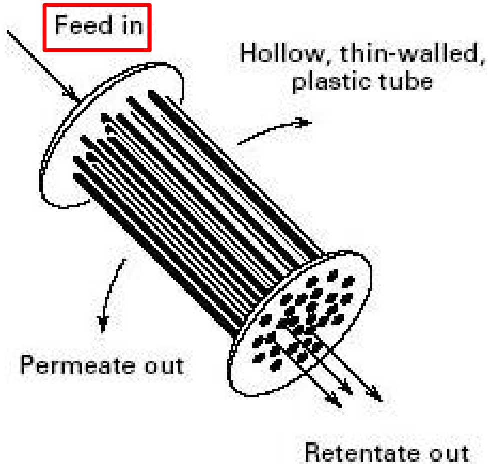
Spiral-wound



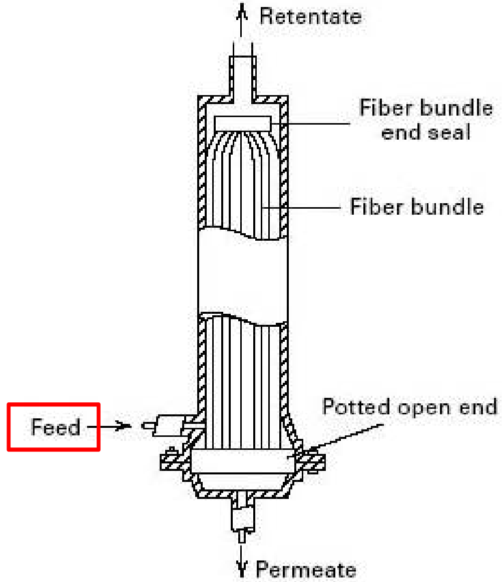
Four-leaf spiral-wound



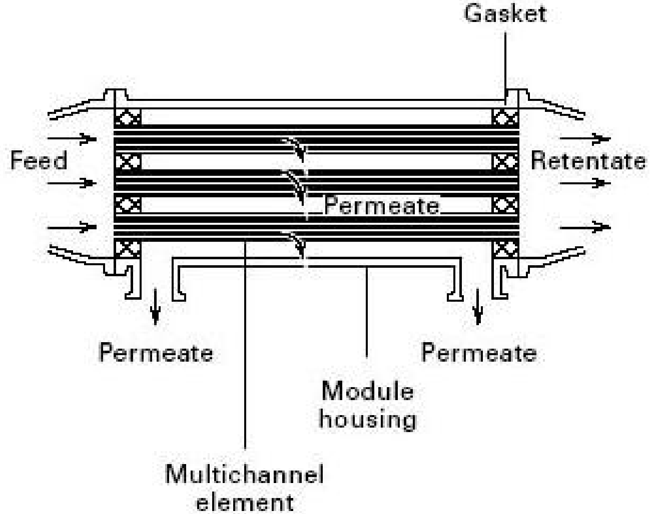
Tubular



Hollow-fiber



Monolithic



Membrane Modules (3)

- Typical characteristics of membrane modules

	Plate and frame	Spiral-wound	Tubular	Hollow-fiber
Packing density, m^2/m^3	30 – 500	200 – 800	30 – 200	500 – 9,000
Resistance to fouling	Good	Moderate	Very good	Poor
Ease of cleaning	Good	Fair	Excellent	Poor
Relative cost	High	Low	High	Low
Main application	D, RO, PV, UF, MF	D, RO, GP, UF, MF	RO, UF	D, RO, GP, UF

D: dialysis, RO: reverse osmosis, GP: gas permeation,
PV: pervaporation, UF: ultrafiltration, MF: microfiltration

- Spiral wound and hollow fiber systems are most popular configurations
- Modules are cascaded in various ways to produce the desired separation