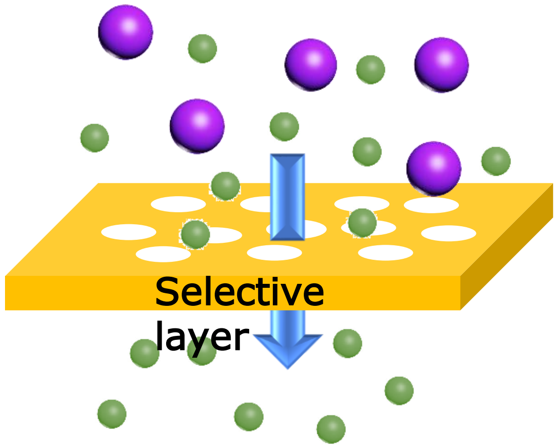
Proses pemisahan 2

Oleh : Indah Prihatiningtyas D.S

1. **Membrane**
2. **Transport through membrane**
3. **Ultrafiltration**
4. **Reverse osmosis**
5. **Gas separation membrane**

PROSES PEMISAHAN

Membrane



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Separation Process

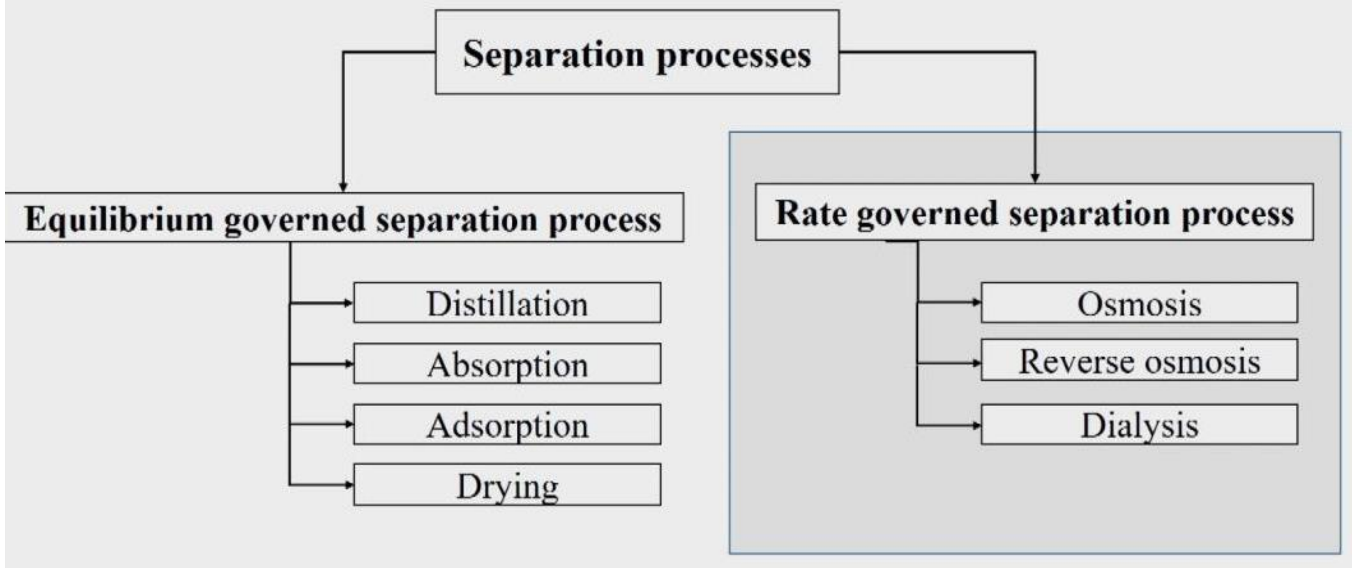
❑ Separation is an "indispensable" part of downstream operation in chemical, petrochemical, biochemical, food and similar allied process industries.

❑ Separation processes of fluid mixtures can be divided into two categories:

i. Equilibrium separation : the product phases are in equilibrium with the feed phases.

- A system is at equilibrium if at constant temperature, pressure and composition the system is stable, not changing with time.
- At equilibrium the chemical potential of the two phase are equal.

ii. Rate governed separation : a difference in rate of physical transport of species brings the separation, i.e., transport of component from a region of higher concentration to lower concentration through some medium under the influence of a driving force.



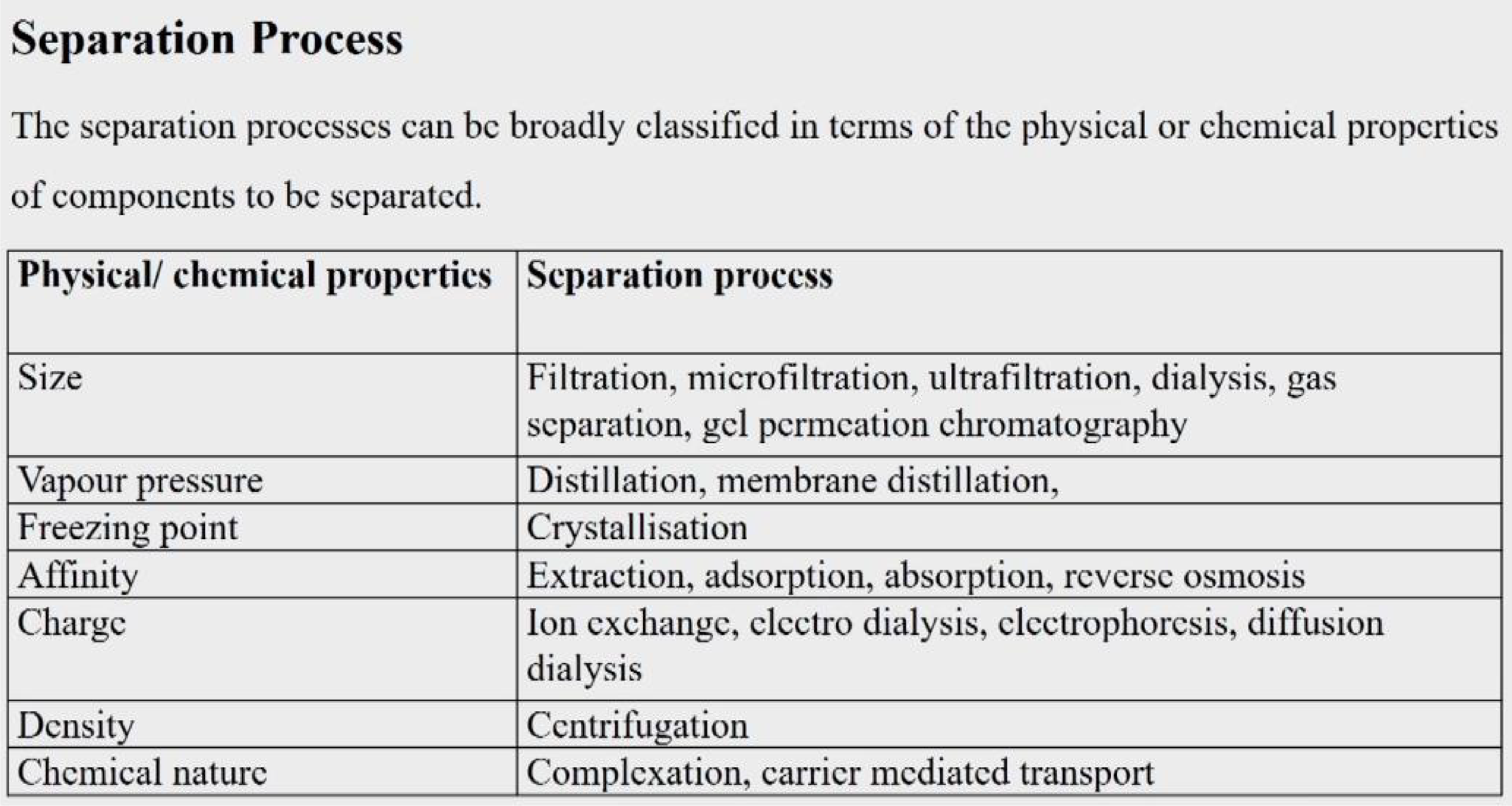
Separation processes

Equilibrium governed separation process

- Distillation
- Absorption
- Adsorption
- Drying

Rate governed separation process

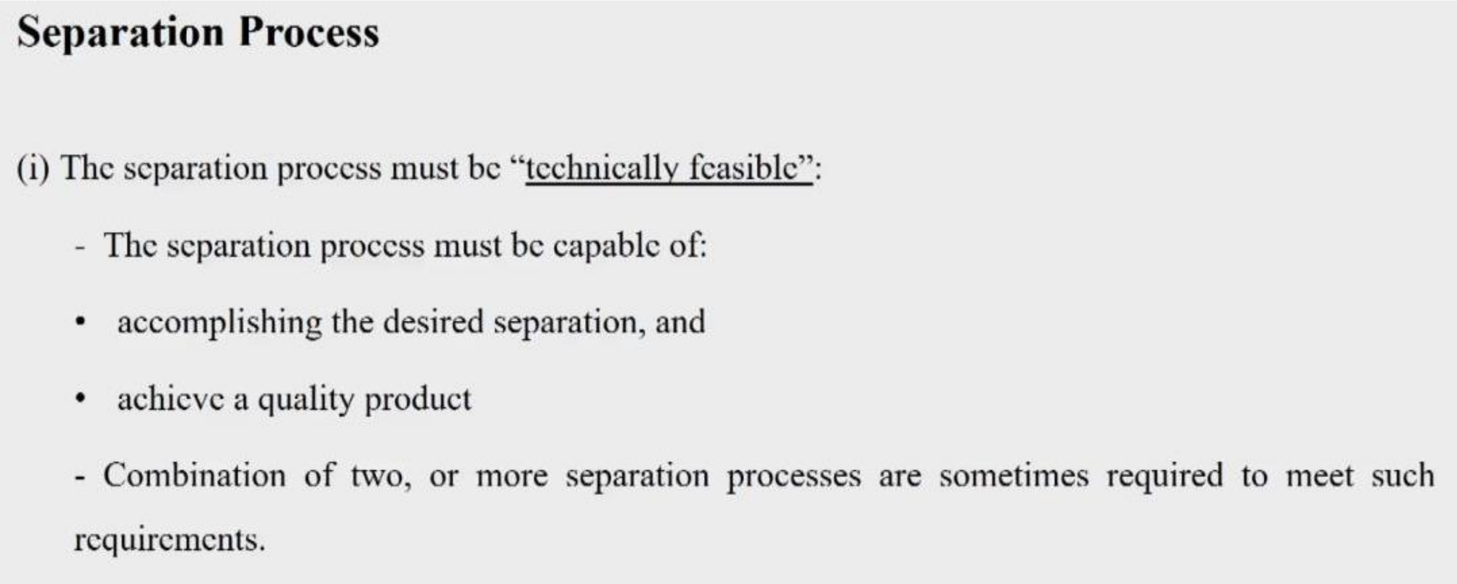
- Osmosis
- Reverse osmosis
- Dialysis



Separation Process

The separation processes can be broadly classified in terms of the physical or chemical properties of components to be separated.

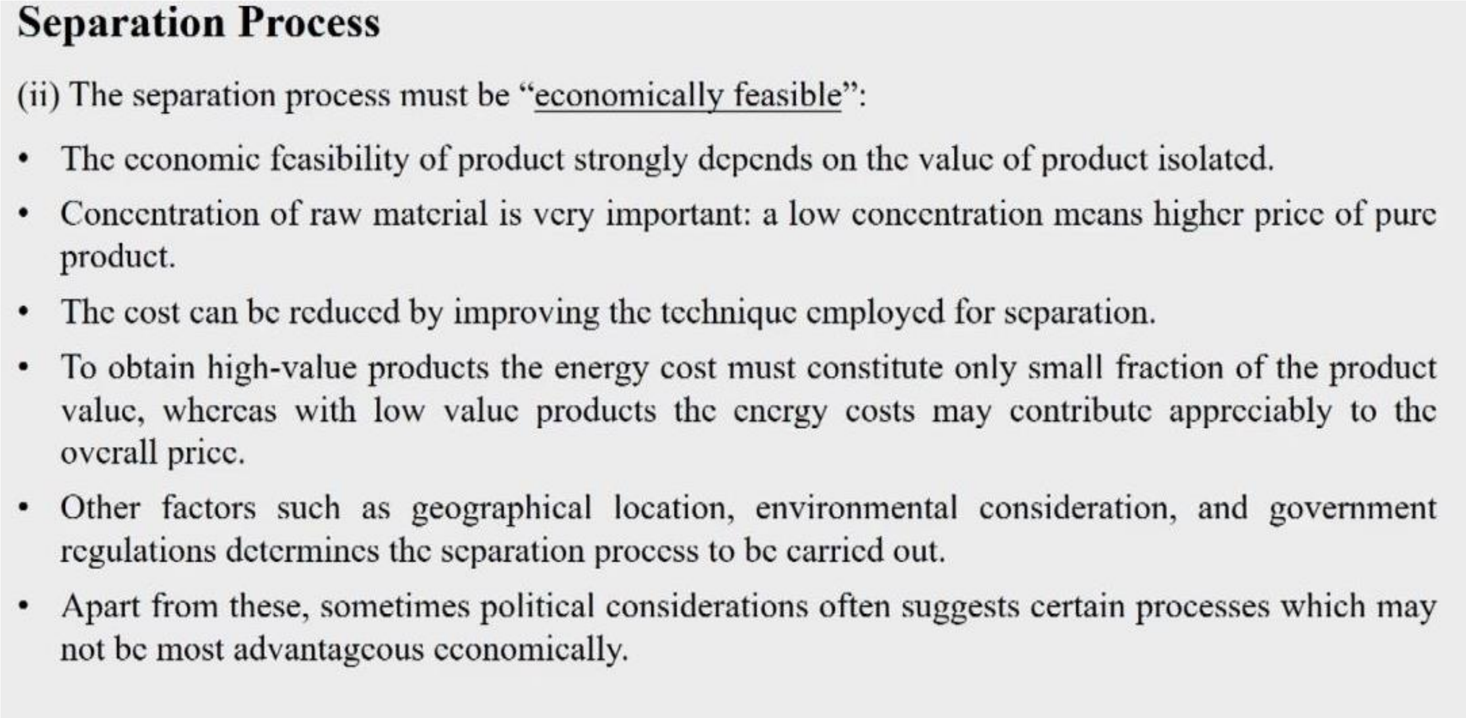
Physical/ chemical properties	**Separation process**
Size	Filtration, microfiltration, ultrafiltration, dialysis, gas separation, gel permeation chromatography
Vapour pressure	Distillation, membrane distillation,
Freezing point	Crystallisation
Affinity	Extraction, adsorption, absorption, reverse osmosis
Charge	Ion exchange, electro dialysis, electrophoresis, diffusion dialysis
Density	Centrifugation
Chemical nature	Complexation, carrier mediated transport



Separation Process

(i) The separation process must be "<u>technically feasible</u>":

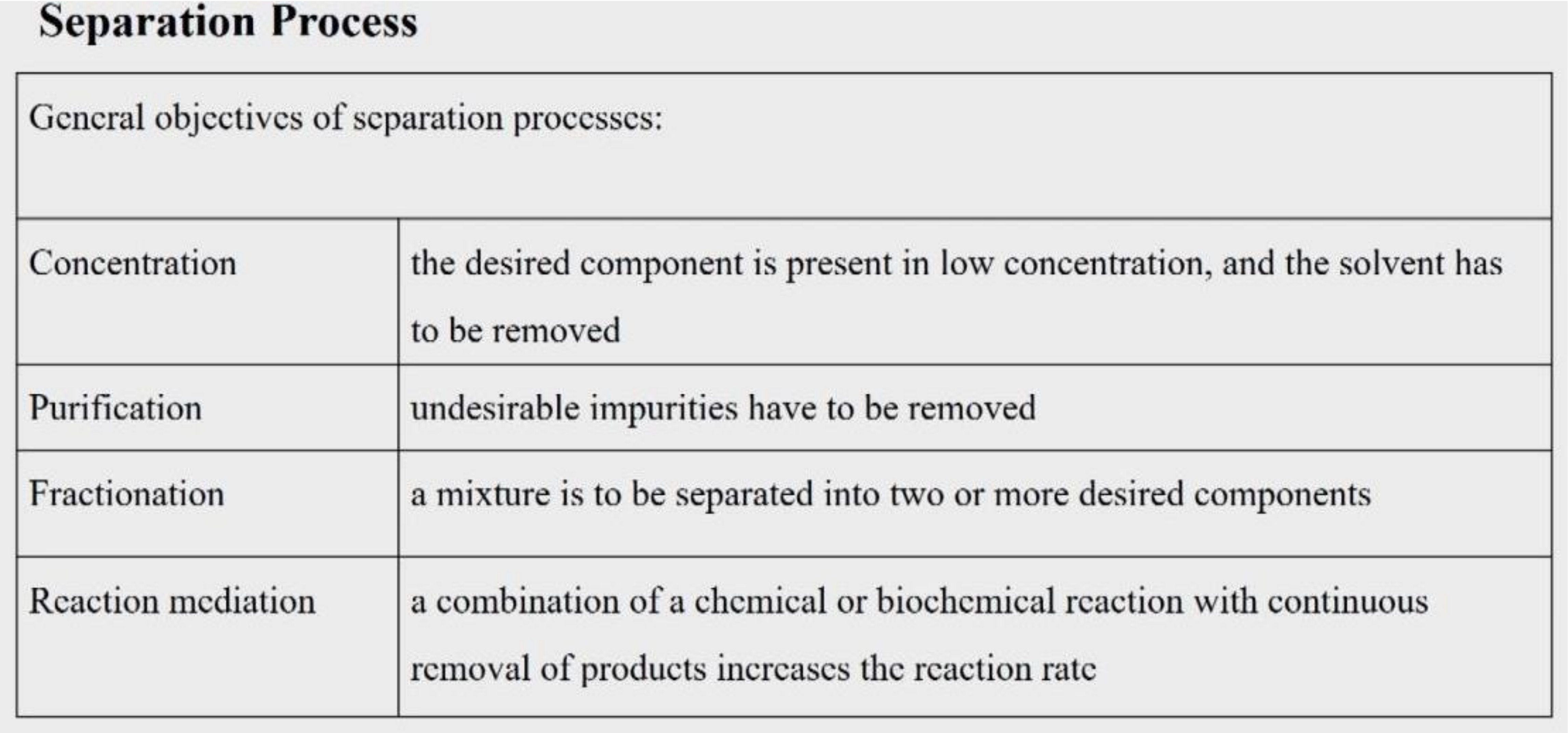
- The separation process must be capable of:
  - accomplishing the desired separation, and
  - achieve a quality product
- Combination of two, or more separation processes are sometimes required to meet such requirements.



Separation Process

(ii) The separation process must be "<u>economically feasible</u>":

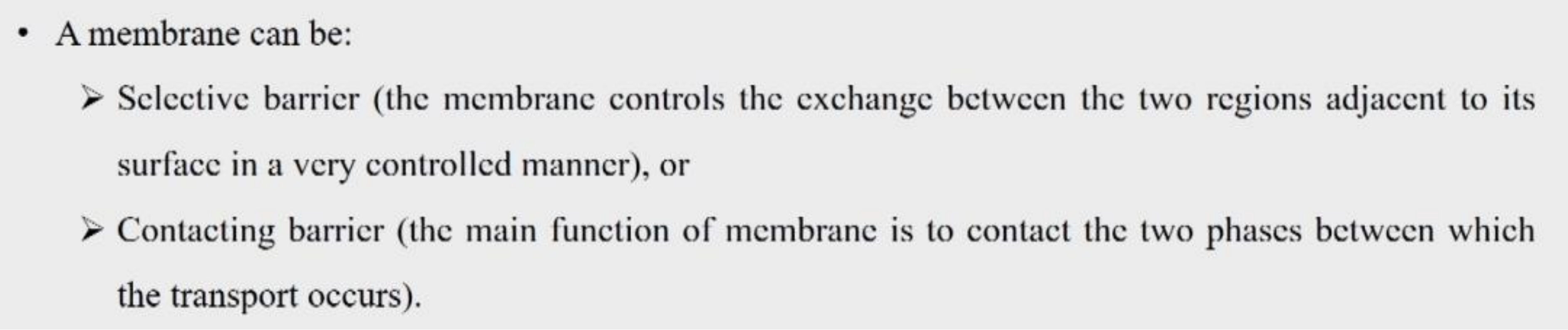
- The economic feasibility of product strongly depends on the value of product isolated.
- Concentration of raw material is very important: a low concentration means higher price of pure product.
- The cost can be reduced by improving the technique employed for separation.
- To obtain high-value products the energy cost must constitute only small fraction of the product value, whereas with low value products the energy costs may contribute appreciably to the overall price.
- Other factors such as geographical location, environmental consideration, and government regulations determines the separation process to be carried out.
- Apart from these, sometimes political considerations often suggests certain processes which may not be most advantageous economically.



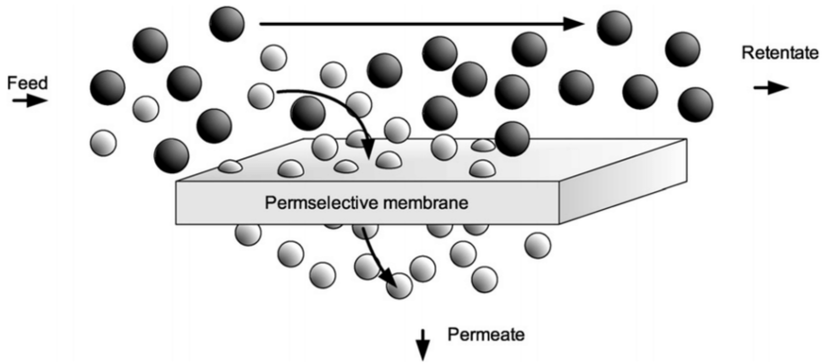
Separation Process

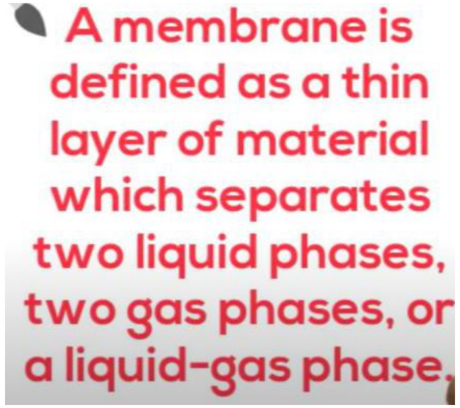
General objectives of separation processes:	
Concentration	the desired component is present in low concentration, and the solvent has to be removed
Purification	undesirable impurities have to be removed
Fractionation	a mixture is to be separated into two or more desired components
Reaction mediation	a combination of a chemical or biochemical reaction with continuous removal of products increases the reaction rate

Membrane



- A membrane can be:
  - Selective barrier (the membrane controls the exchange between the two regions adjacent to its surface in a very controlled manner), or
  - Contacting barrier (the main function of membrane is to contact the two phases between which the transport occurs).



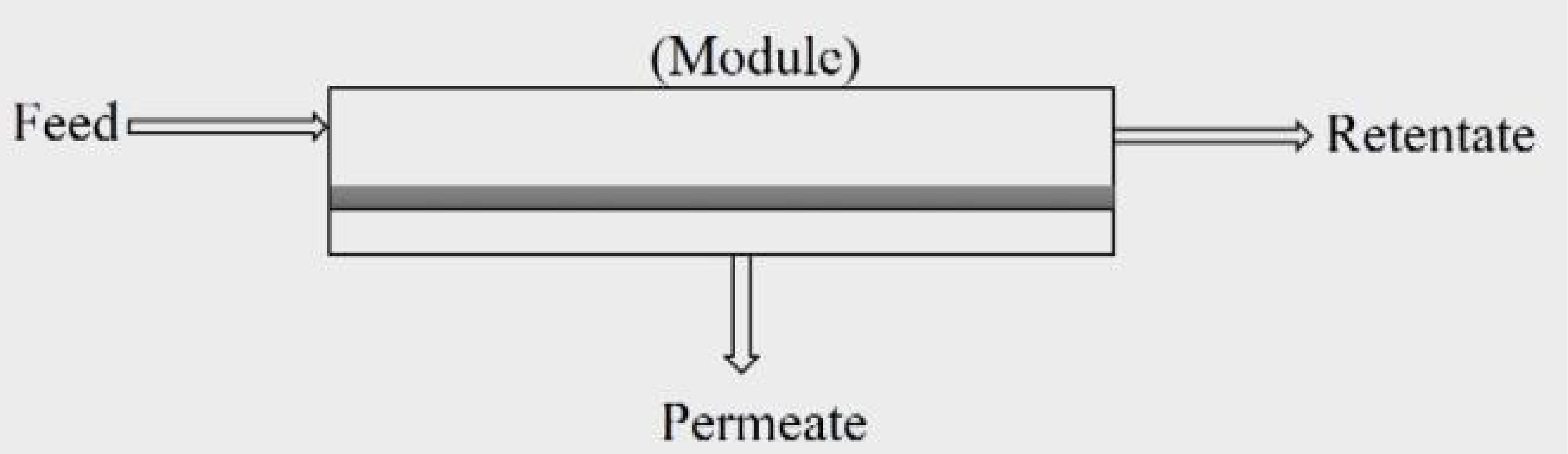


A membrane is defined as a thin layer of material which separates two liquid phases, two gas phases, or a liquid-gas phase.

Membrane-based proses sebagian besar adalah rate governed. Intinya pada perbedaan perpindahan komponen/species melalui membrane

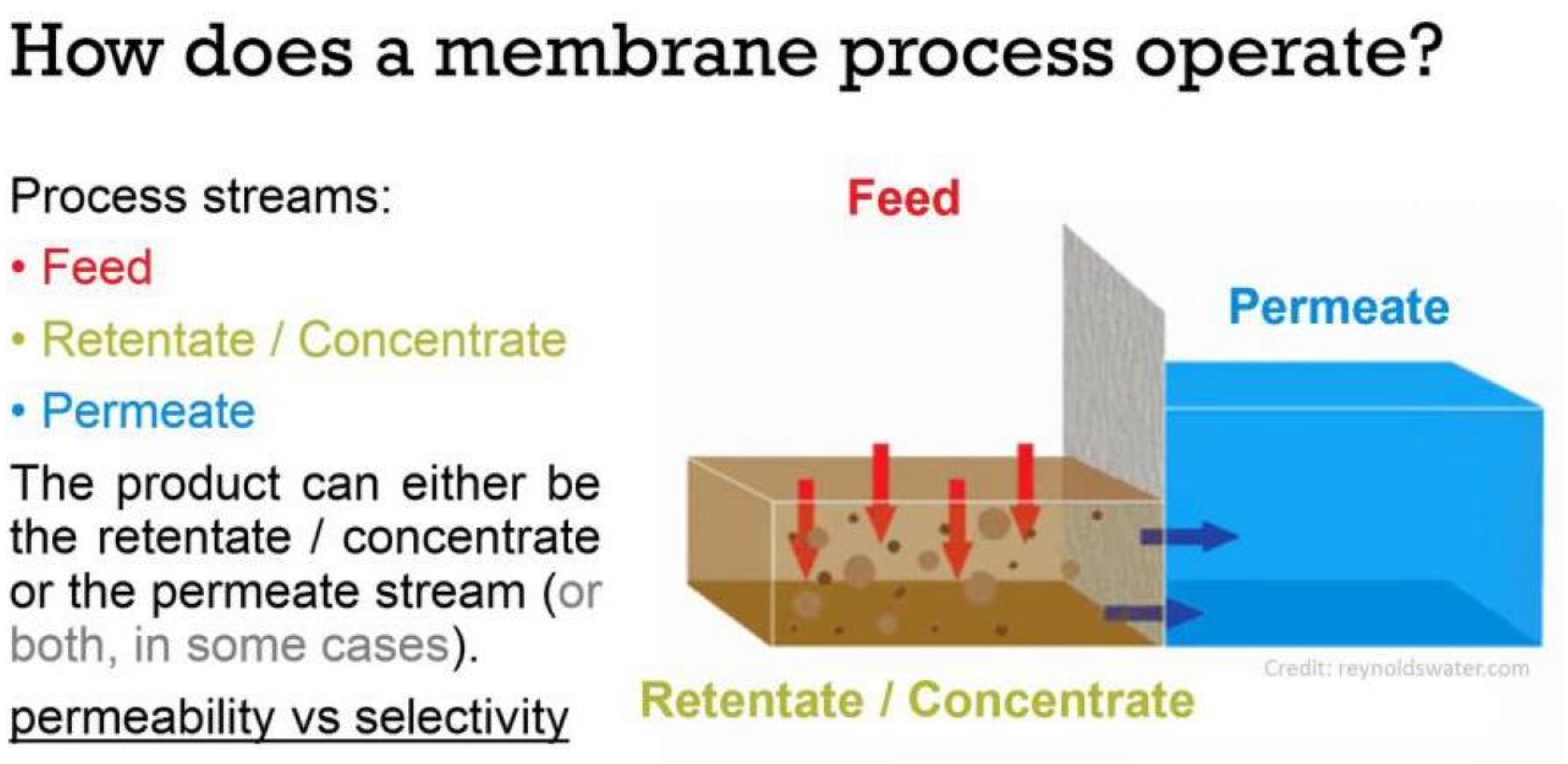
Pemisahan tercapai karena membrane memiliki kemampuan untuk memindahkan suatu komponen dari campuran di feed lebih mudah dari komponen lain.

Membrane



Tujuan proses pemisahan dengan membrane :

- Konsentrasi : produk adalah di retentate
- Pemurnian/purification : tergantung dari pengotor yang ingin dihilangkan sehingga produk bisa retentate atau permeate



How does a membrane process operate?

Process streams:

- Feed
- Retentate / Concentrate
- Permeate

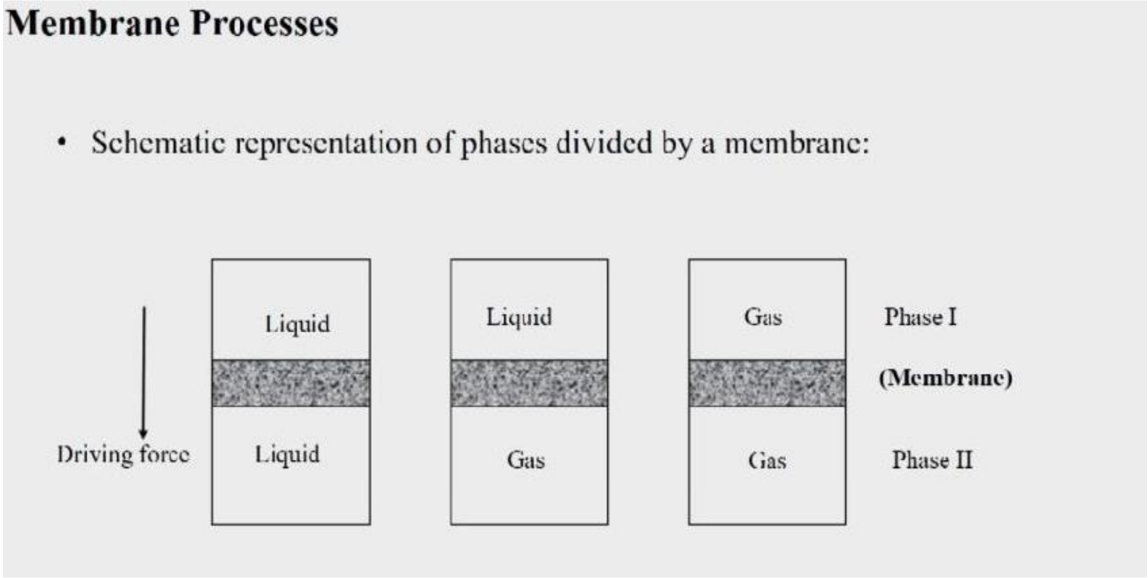
The product can either be the retentate / concentrate or the permeate stream (or both, in some cases).

permeability vs selectivity

Credit: reynoldswater.com

- Membrane merupakan “the heart”
- In membrane processes, it can be considered as perm-selective barrier or interface between two phases

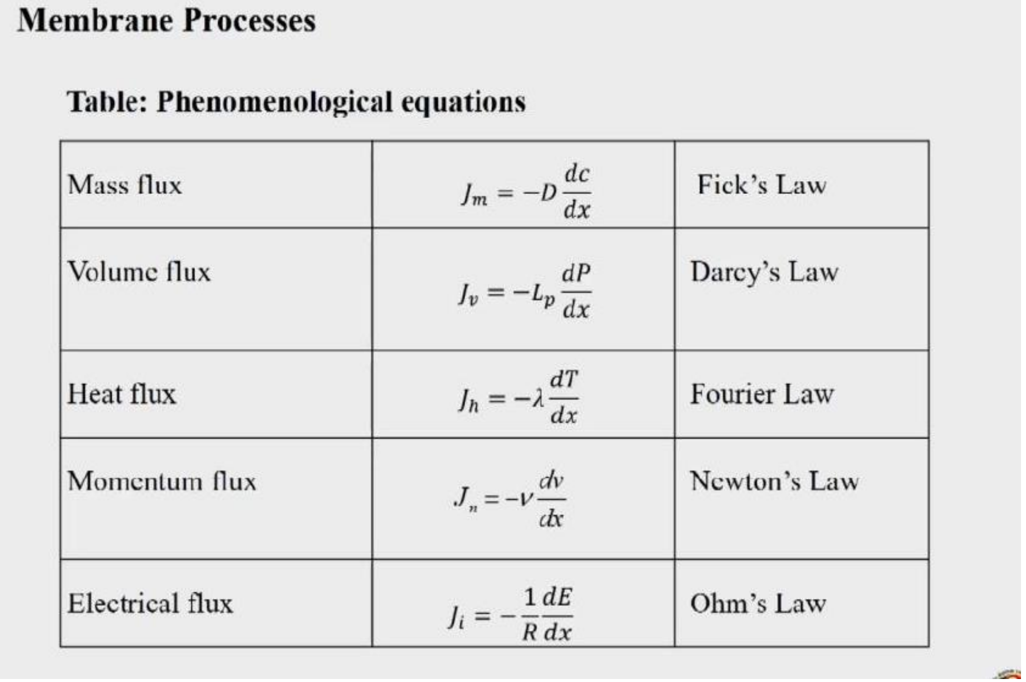
Proses pemisahan – Membrane



Membrane Processes

- Schematic representation of phases divided by a membrane:

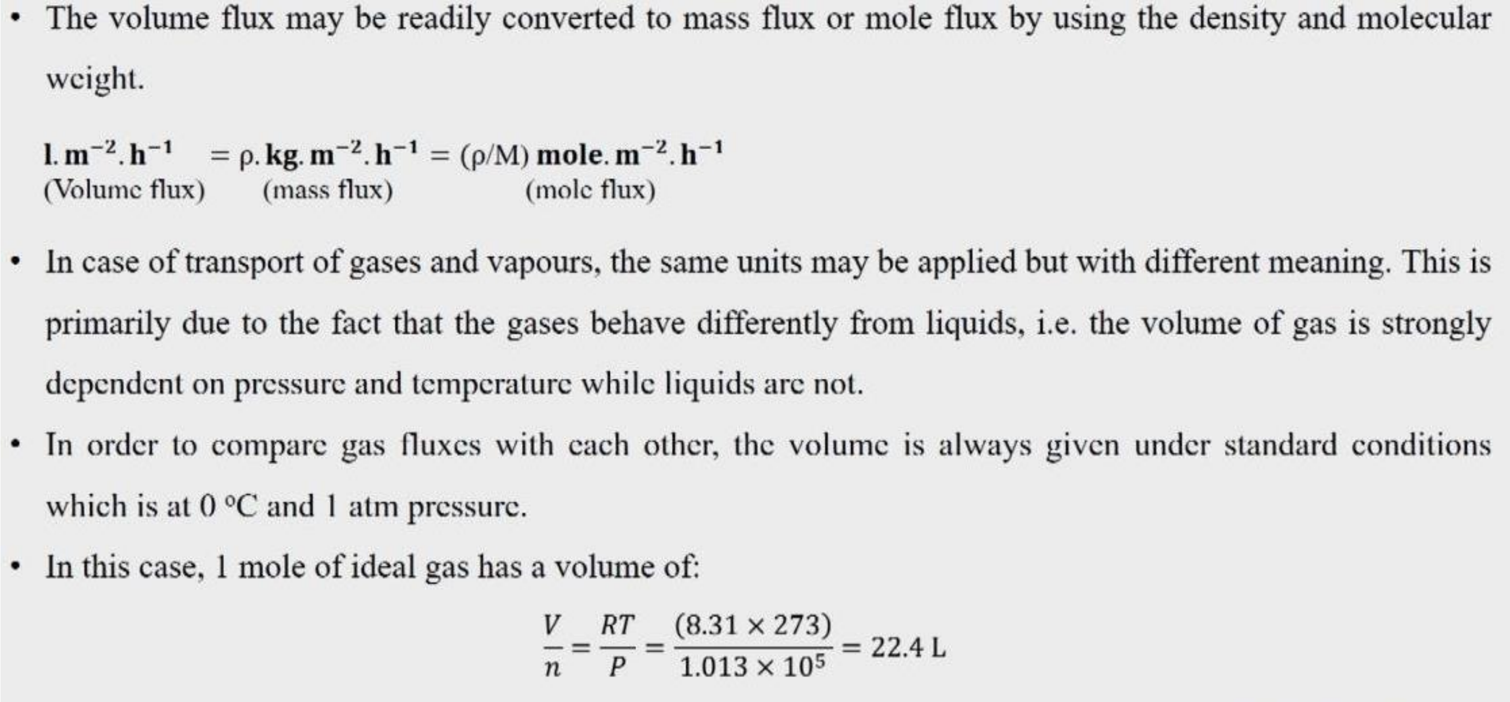
- Parameter dari performance /kinerja membrane adalah : a) selectivity dan b) flow through the membrane (laju aliran).
- The term flow through membrane : *Flux or permeation rate*.
- Flux : the volume flowing through the membrane per unit area and time.



Membrane Processes

Table: Phenomenological equations

Mass flux	$J_m = -D\frac{dc}{dx}$	Fick's Law
Volume flux	$J_v = -L_p\frac{dP}{dx}$	Darcy's Law
Heat flux	$J_h = -\lambda\frac{dT}{dx}$	Fourier Law
Momentum flux	$J_n = -\nu\frac{dv}{dx}$	Newton's Law
Electrical flux	$J_i = -\frac{1}{R}\frac{dE}{dx}$	Ohm's Law

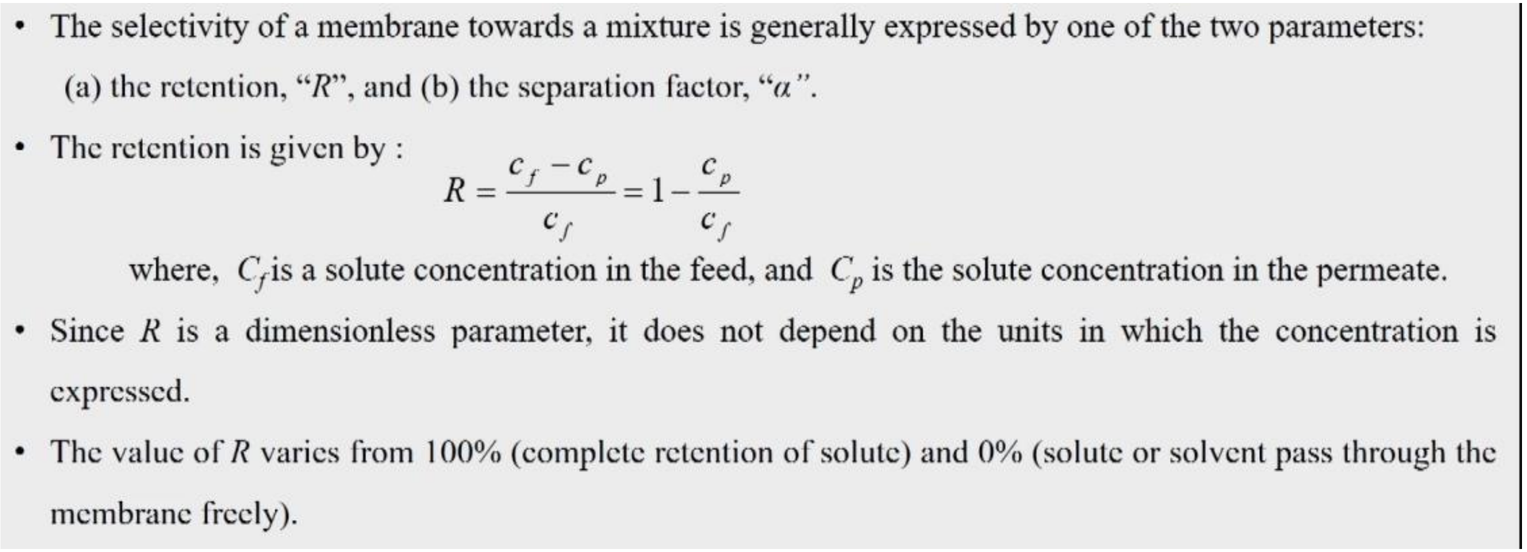


- The volume flux may be readily converted to mass flux or mole flux by using the density and molecular weight.

$$\underset{\text{(Volume flux)}}{\mathbf{l.m^{-2}.h^{-1}}} = \underset{\text{(mass flux)}}{\rho.\mathbf{kg.m^{-2}.h^{-1}}} = \underset{\text{(mole flux)}}{(\rho/M)\,\mathbf{mole.m^{-2}.h^{-1}}}$$

- In case of transport of gases and vapours, the same units may be applied but with different meaning. This is primarily due to the fact that the gases behave differently from liquids, i.e. the volume of gas is strongly dependent on pressure and temperature while liquids are not.
- In order to compare gas fluxes with each other, the volume is always given under standard conditions which is at 0 °C and 1 atm pressure.
- In this case, 1 mole of ideal gas has a volume of:

$$\frac{V}{n} = \frac{RT}{P} = \frac{(8.31 \times 273)}{1.013 \times 10^5} = 22.4\ \text{L}$$

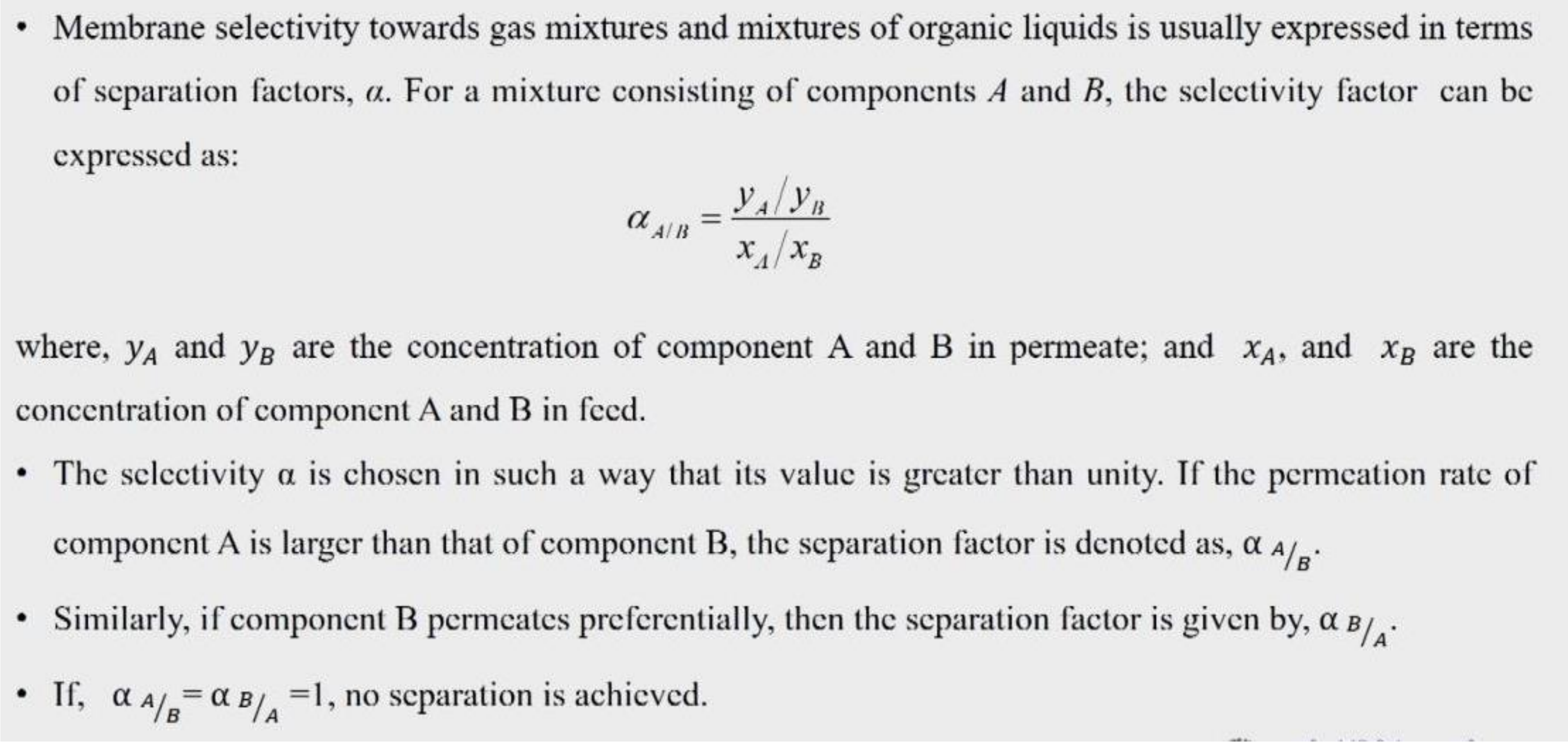


- The selectivity of a membrane towards a mixture is generally expressed by one of the two parameters: (a) the retention, "*R*", and (b) the separation factor, "*α*".
- The retention is given by :

$$R = \frac{c_f - c_p}{c_f} = 1 - \frac{c_p}{c_f}$$

where, C_f is a solute concentration in the feed, and C_p is the solute concentration in the permeate.

- Since *R* is a dimensionless parameter, it does not depend on the units in which the concentration is expressed.
- The value of *R* varies from 100% (complete retention of solute) and 0% (solute or solvent pass through the membrane freely).

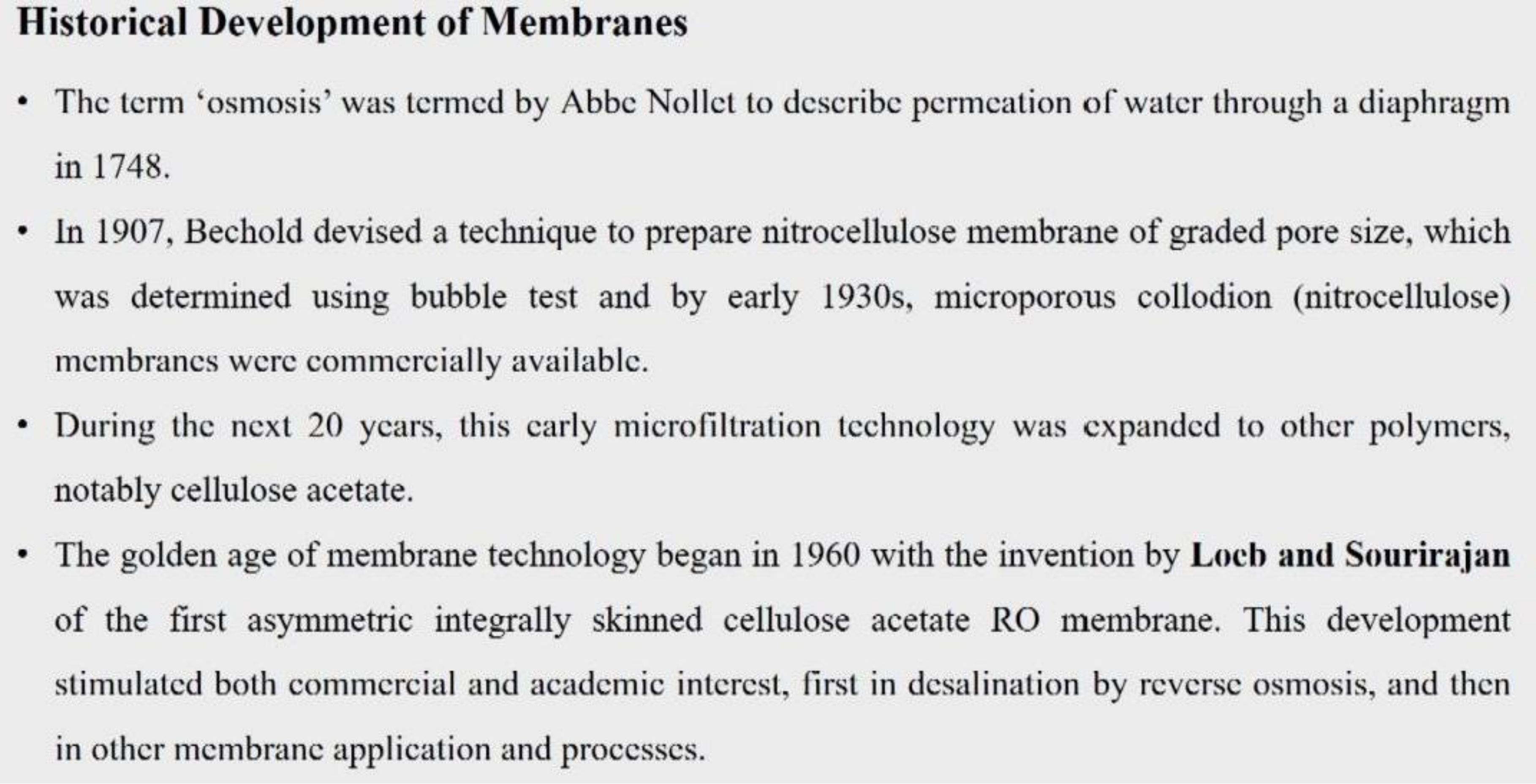


- Membrane selectivity towards gas mixtures and mixtures of organic liquids is usually expressed in terms of separation factors, α. For a mixture consisting of components A and B, the selectivity factor can be expressed as:

$$\alpha_{A/B} = \frac{y_A / y_B}{x_A / x_B}$$

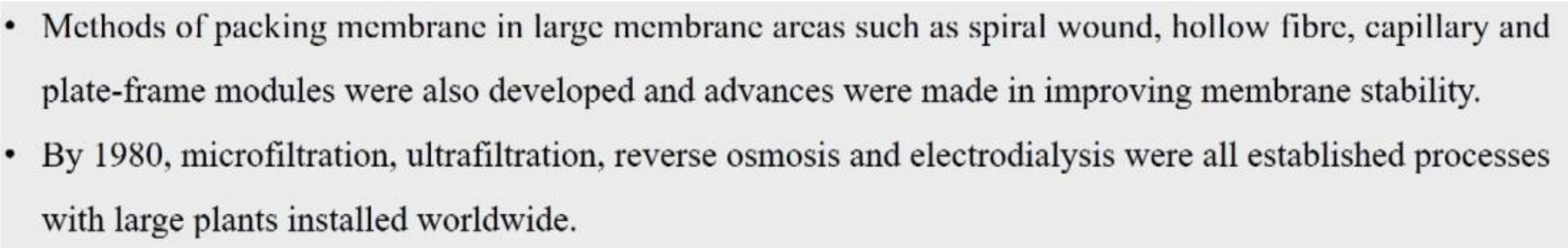
where, y_A and y_B are the concentration of component A and B in permeate; and x_A, and x_B are the concentration of component A and B in feed.

- The selectivity α is chosen in such a way that its value is greater than unity. If the permeation rate of component A is larger than that of component B, the separation factor is denoted as, $\alpha_{A/B}$.
- Similarly, if component B permeates preferentially, then the separation factor is given by, $\alpha_{B/A}$.
- If, $\alpha_{A/B} = \alpha_{B/A} = 1$, no separation is achieved.

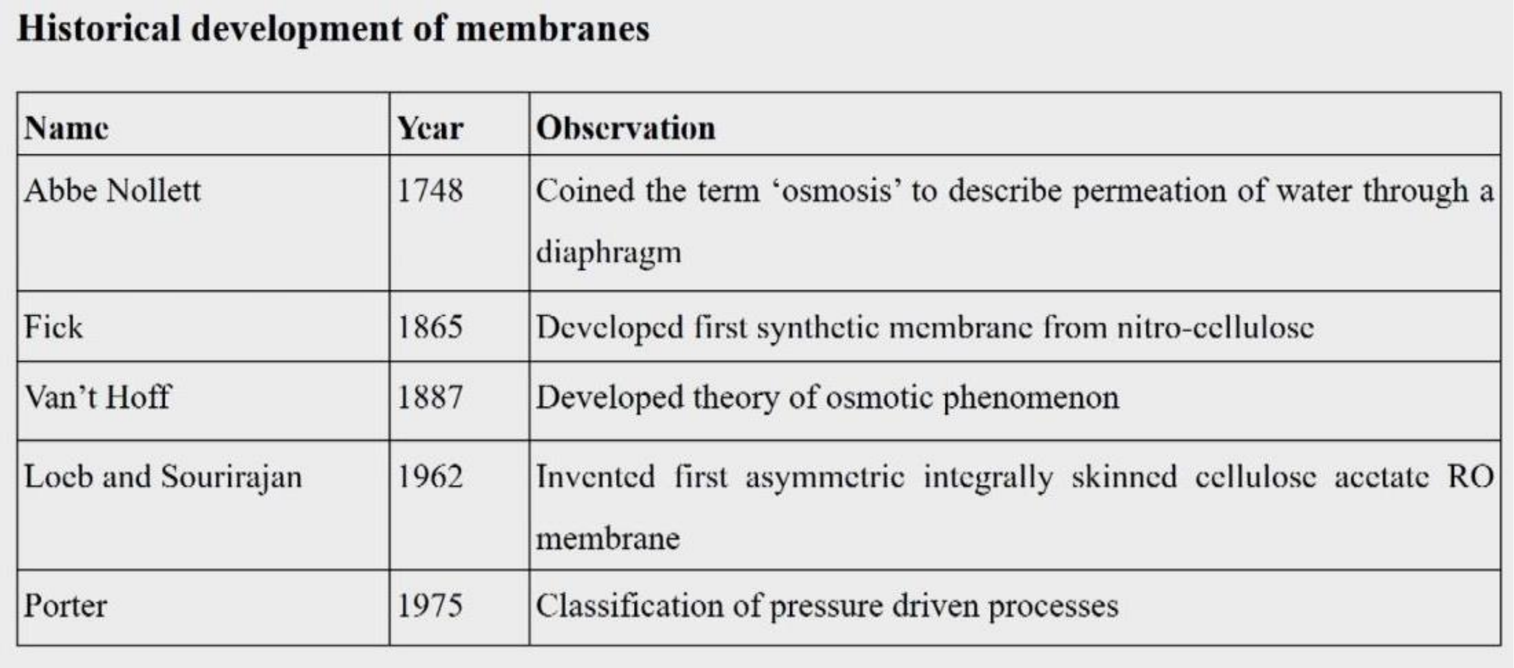


Historical Development of Membranes

- The term ‘osmosis’ was termed by Abbe Nollet to describe permeation of water through a diaphragm in 1748.
- In 1907, Bechold devised a technique to prepare nitrocellulose membrane of graded pore size, which was determined using bubble test and by early 1930s, microporous collodion (nitrocellulose) membranes were commercially available.
- During the next 20 years, this early microfiltration technology was expanded to other polymers, notably cellulose acetate.
- The golden age of membrane technology began in 1960 with the invention by **Loeb and Sourirajan** of the first asymmetric integrally skinned cellulose acetate RO membrane. This development stimulated both commercial and academic interest, first in desalination by reverse osmosis, and then in other membrane application and processes.

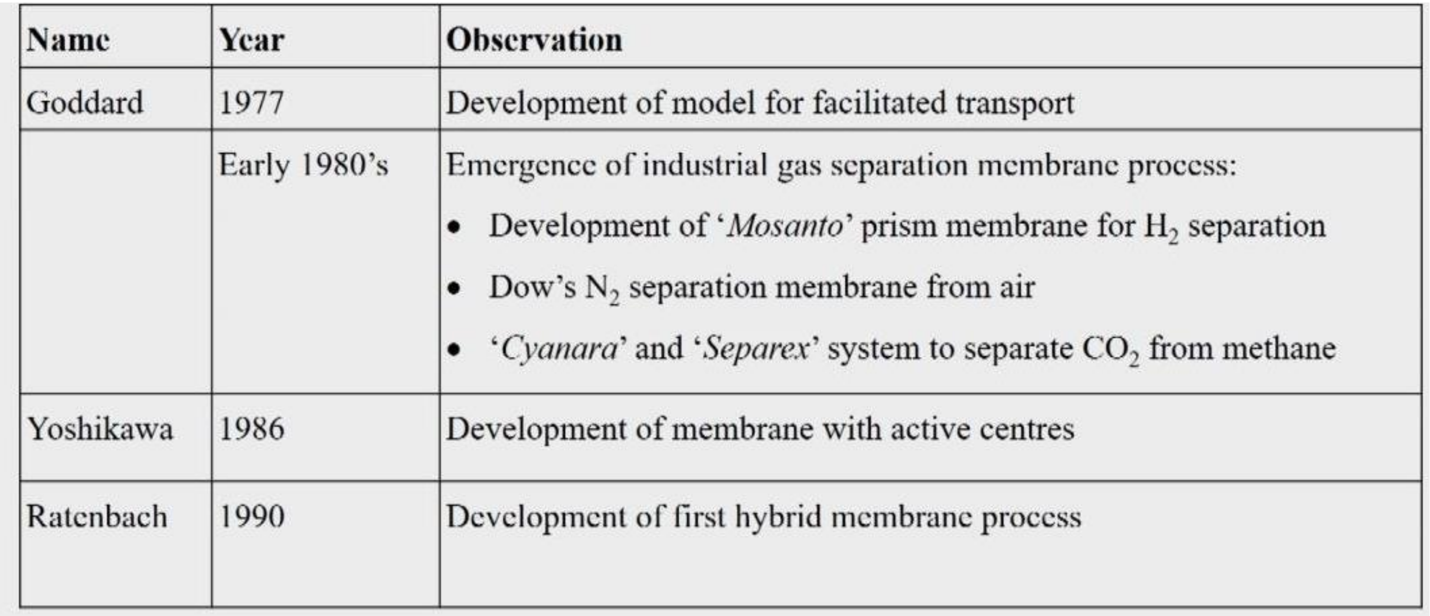


- Methods of packing membrane in large membrane areas such as spiral wound, hollow fibre, capillary and plate-frame modules were also developed and advances were made in improving membrane stability.
- By 1980, microfiltration, ultrafiltration, reverse osmosis and electrodialysis were all established processes with large plants installed worldwide.

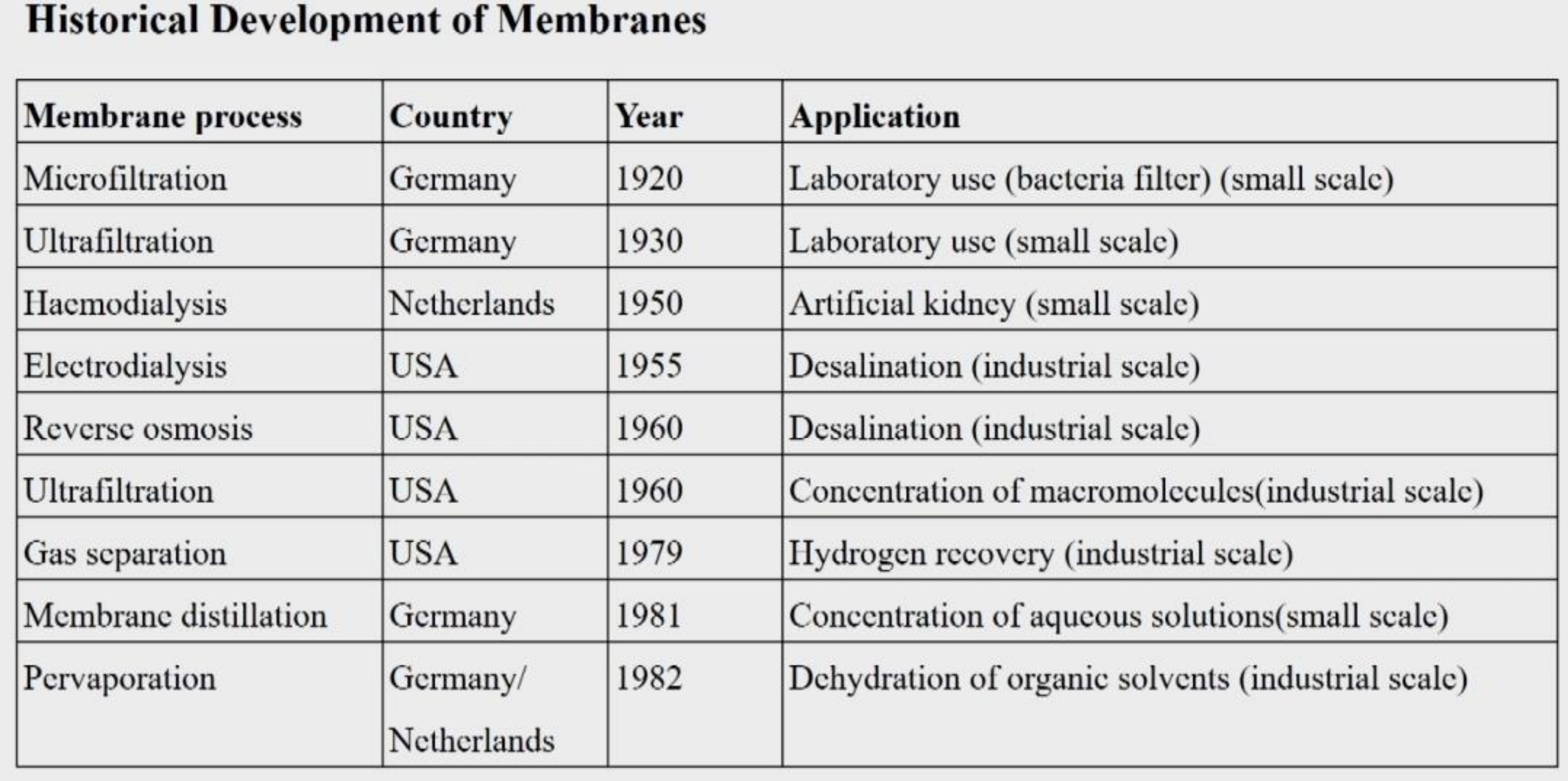


Historical development of membranes

Name	Year	Observation
Abbe Nollett	1748	Coined the term ‘osmosis’ to describe permeation of water through a diaphragm
Fick	1865	Developed first synthetic membrane from nitro-cellulose
Van’t Hoff	1887	Developed theory of osmotic phenomenon
Loeb and Sourirajan	1962	Invented first asymmetric integrally skinned cellulose acetate RO membrane
Porter	1975	Classification of pressure driven processes

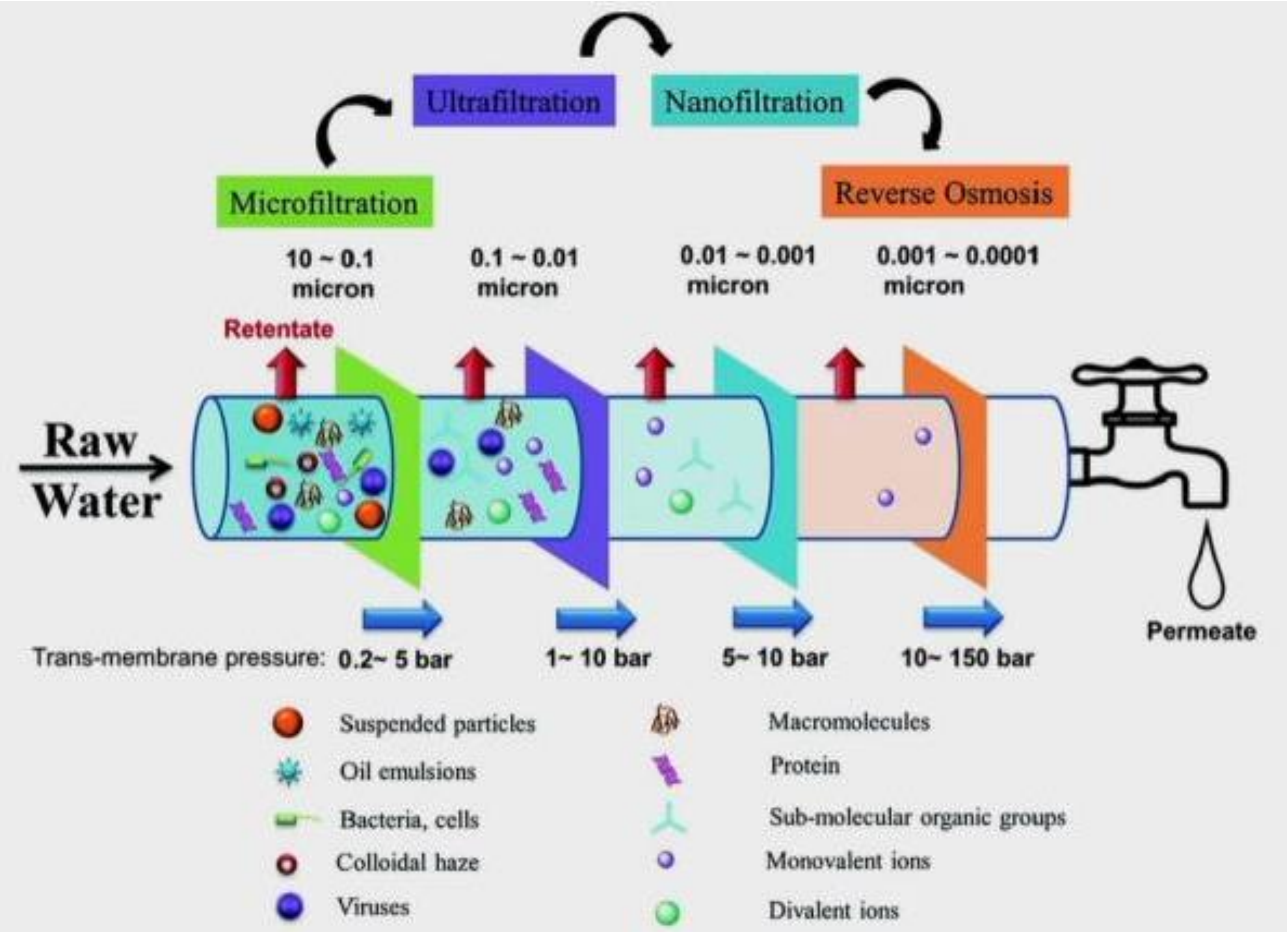


Name	Year	Observation
Goddard	1977	Development of model for facilitated transport
	Early 1980’s	Emergence of industrial gas separation membrane process: • Development of ‘*Mosanto*’ prism membrane for H_2 separation • Dow’s N_2 separation membrane from air • ‘*Cyanara*’ and ‘*Separex*’ system to separate CO_2 from methane
Yoshikawa	1986	Development of membrane with active centres
Ratenbach	1990	Development of first hybrid membrane process



Historical Development of Membranes

Membrane process	Country	Year	Application
Microfiltration	Germany	1920	Laboratory use (bacteria filter) (small scale)
Ultrafiltration	Germany	1930	Laboratory use (small scale)
Haemodialysis	Netherlands	1950	Artificial kidney (small scale)
Electrodialysis	USA	1955	Desalination (industrial scale)
Reverse osmosis	USA	1960	Desalination (industrial scale)
Ultrafiltration	USA	1960	Concentration of macromolecules(industrial scale)
Gas separation	USA	1979	Hydrogen recovery (industrial scale)
Membrane distillation	Germany	1981	Concentration of aqueous solutions(small scale)
Pervaporation	Germany/ Netherlands	1982	Dehydration of organic solvents (industrial scale)


Ultrafiltration
Nanofiltration
Microfiltration
Reverse Osmosis
10 ~ 0.1 micron
0.1 ~ 0.01 micron
0.01 ~ 0.001 micron
0.001 ~ 0.0001 micron
Retentate
Raw Water
Permeate
Trans-membrane pressure: 0.2~ 5 bar
1~ 10 bar
5~ 10 bar
10~ 150 bar
Suspended particles
Oil emulsions
Bacteria, cells
Colloidal haze
Viruses
Macromolecules
Protein
Sub-molecular organic groups
Monovalent ions
Divalent ions

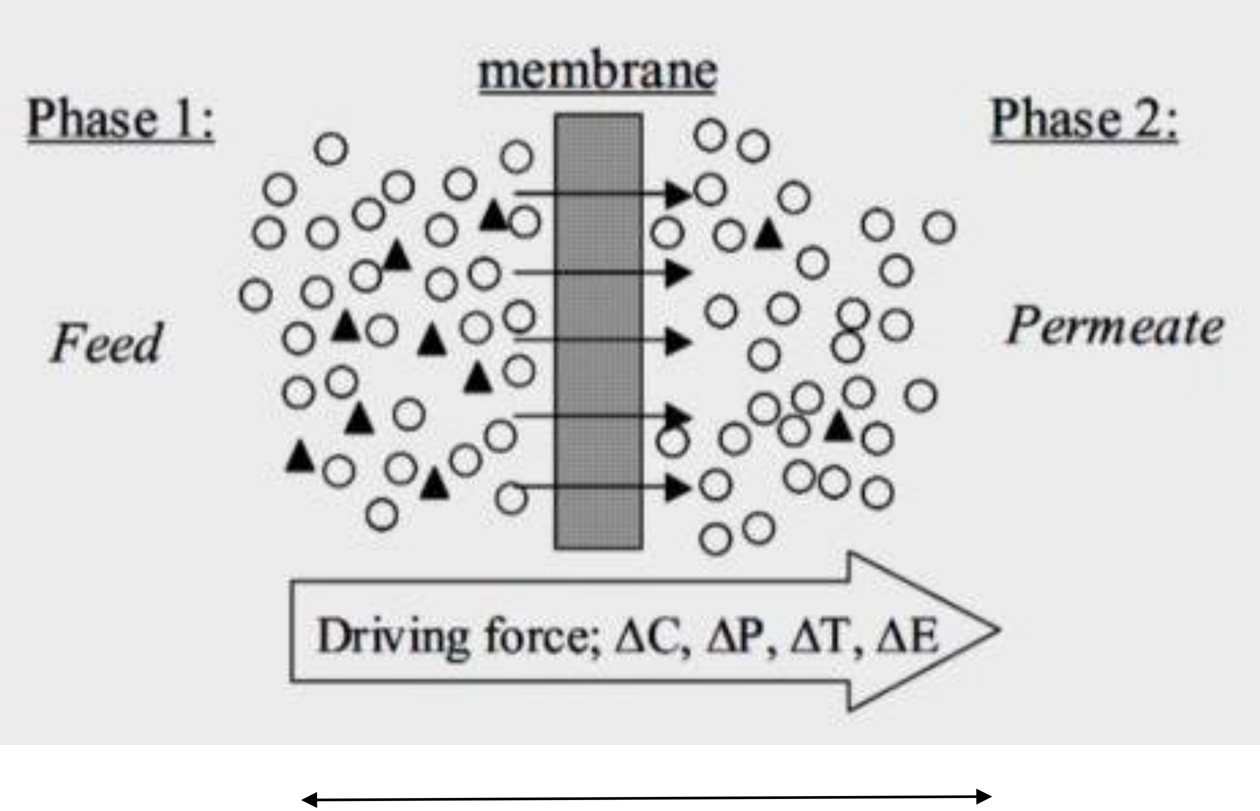
What drives a membrane process?

Transport Phenomena

involves the movement of mass, momentum, or energy through a medium

$$\text{Flux} \propto \frac{\textbf{Driving Force}}{\text{Resistance}}$$

“transfer rate per unit area”

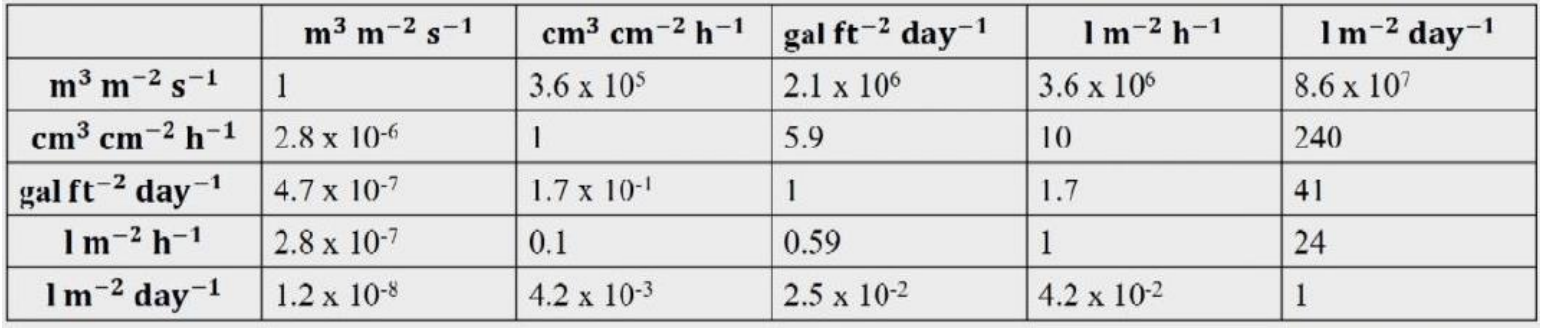


Δμ (chemical potential)

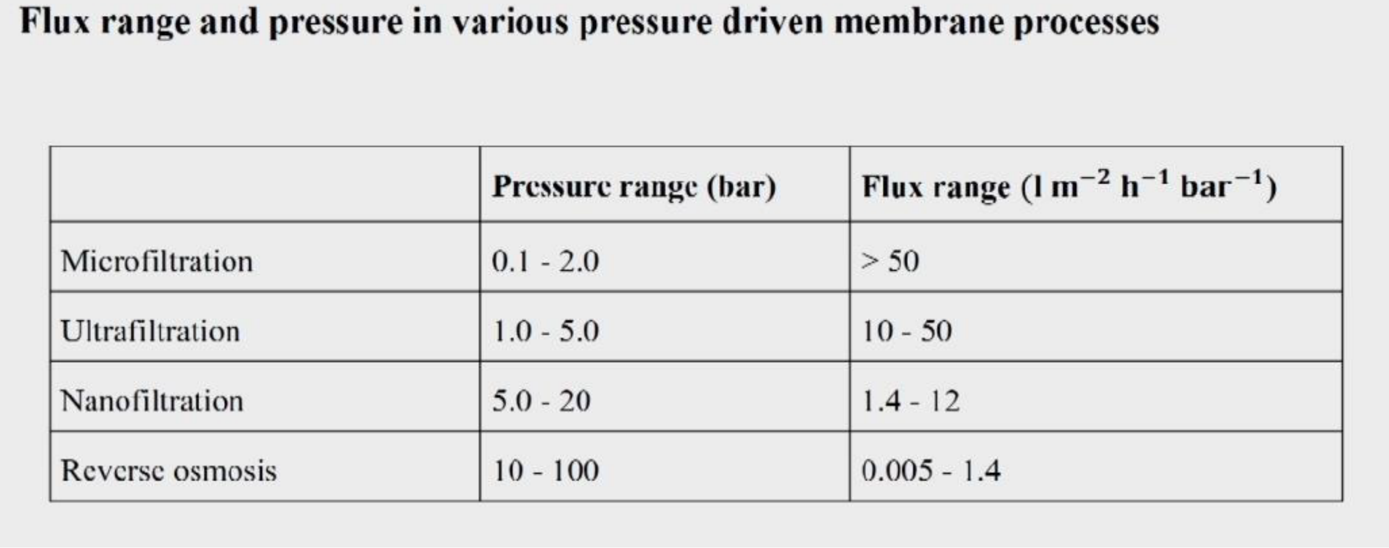
Some membrane process and their driving force

Membrane process	**Phase I**	**Phase II**	**Driving force**
Microfiltration	L	L	ΔP
Ultrafiltration	L	L	ΔP
Nanofiltration	L	L	ΔP
Reverse osmosis	L	L	ΔP
Piezodialysis	L	L	ΔP
Gas separation	G	G	ΔP
Vapour permeation	G	G	ΔP
Pervaporation	L	G	ΔP
Electrodialysis	L	L	ΔE
Membrane electrodialysis	L	L	ΔE
Dialysis	L	L	ΔC
Diffusion dialysis	L	L	ΔC
Thermo-osmosis	L	L	$\Delta T/\Delta P$
Membrane distillation	L	L	$\Delta T/\Delta P$

Table konversi flux



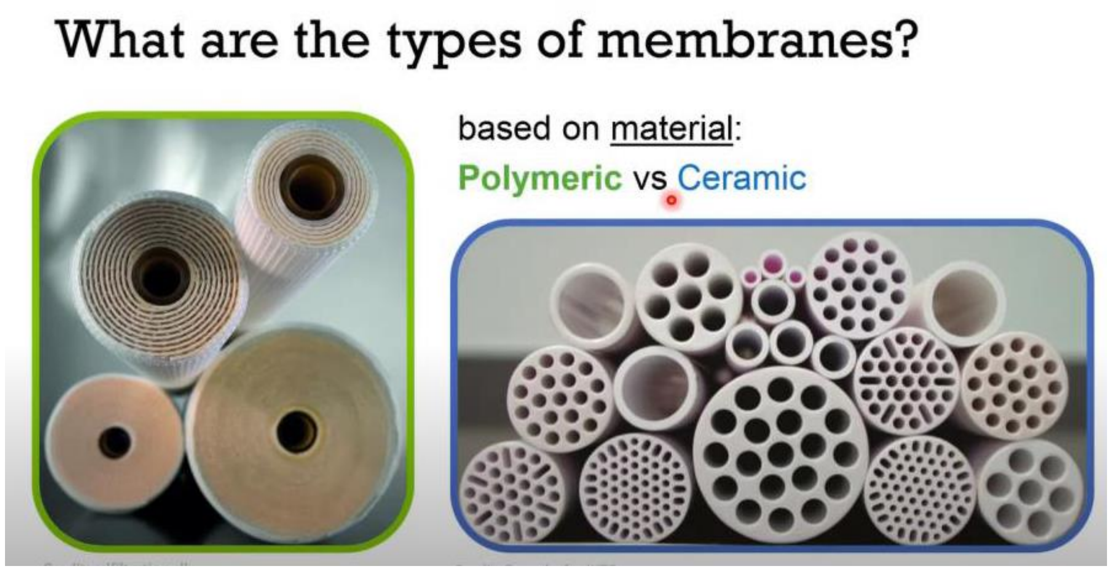
	$m^3\,m^{-2}\,s^{-1}$	$cm^3\,cm^{-2}\,h^{-1}$	$gal\,ft^{-2}\,day^{-1}$	$l\,m^{-2}\,h^{-1}$	$l\,m^{-2}\,day^{-1}$
$m^3\,m^{-2}\,s^{-1}$	1	3.6×10^{5}	2.1×10^{6}	3.6×10^{6}	8.6×10^{7}
$cm^3\,cm^{-2}\,h^{-1}$	2.8×10^{-6}	1	5.9	10	240
$gal\,ft^{-2}\,day^{-1}$	4.7×10^{-7}	1.7×10^{-1}	1	1.7	41
$l\,m^{-2}\,h^{-1}$	2.8×10^{-7}	0.1	0.59	1	24
$l\,m^{-2}\,day^{-1}$	1.2×10^{-8}	4.2×10^{-3}	2.5×10^{-2}	4.2×10^{-2}	1



Flux range and pressure in various pressure driven membrane processes

	Pressure range (bar)	Flux range ($l\,m^{-2}\,h^{-1}\,bar^{-1}$)
Microfiltration	0.1 - 2.0	> 50
Ultrafiltration	1.0 - 5.0	10 - 50
Nanofiltration	5.0 - 20	1.4 - 12
Reverse osmosis	10 - 100	0.005 - 1.4

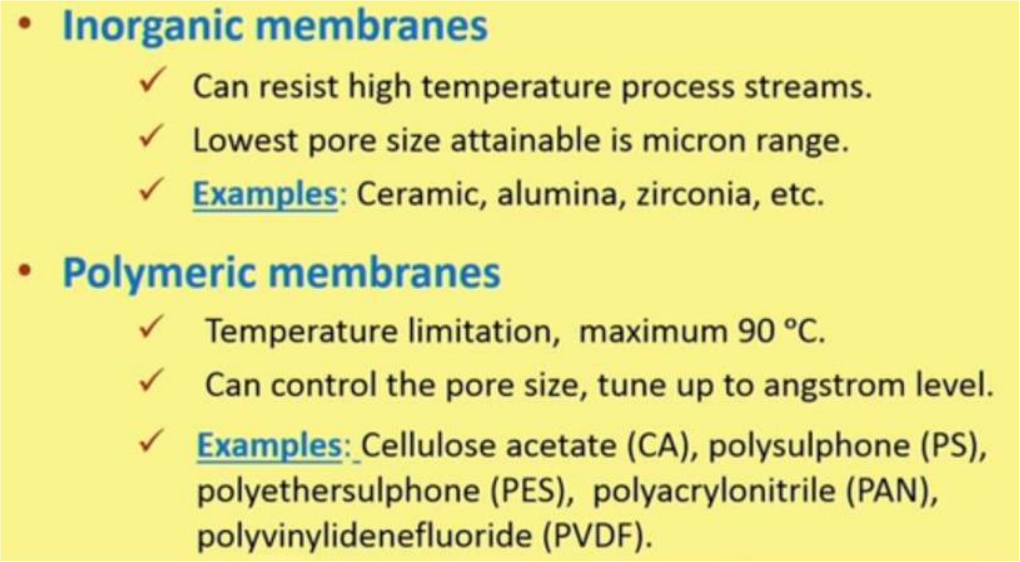
Membrane material



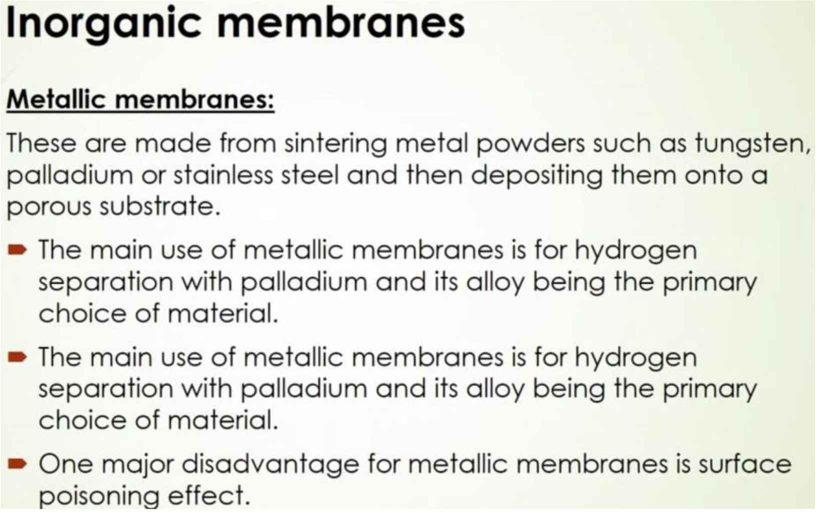
What are the types of membranes?

based on material:

Polymeric vs Ceramic



- **Inorganic membranes**
  - ✓ Can resist high temperature process streams.
  - ✓ Lowest pore size attainable is micron range.
  - ✓ Examples: Ceramic, alumina, zirconia, etc.
- **Polymeric membranes**
  - ✓ Temperature limitation, maximum 90 °C.
  - ✓ Can control the pore size, tune up to angstrom level.
  - ✓ Examples: Cellulose acetate (CA), polysulphone (PS), polyethersulphone (PES), polyacrylonitrile (PAN), polyvinylidenefluoride (PVDF).



Inorganic membranes

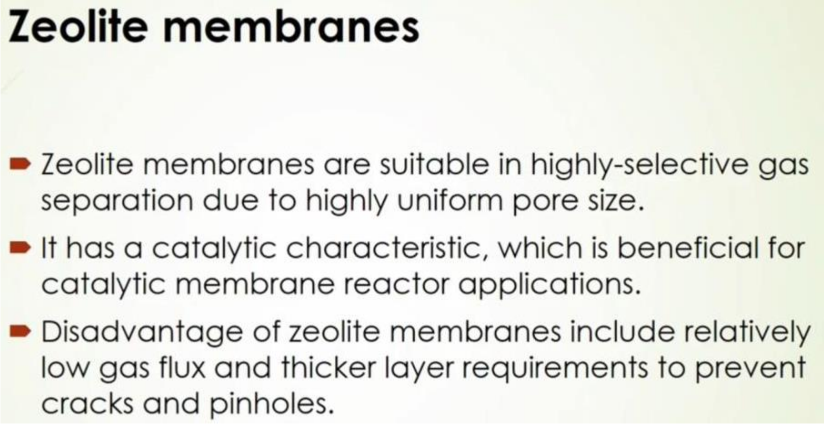
Metallic membranes:

These are made from sintering metal powders such as tungsten, palladium or stainless steel and then depositing them onto a porous substrate.

- The main use of metallic membranes is for hydrogen separation with palladium and its alloy being the primary choice of material.
- The main use of metallic membranes is for hydrogen separation with palladium and its alloy being the primary choice of material.
- One major disadvantage for metallic membranes is surface poisoning effect.

Ceramic membranes:

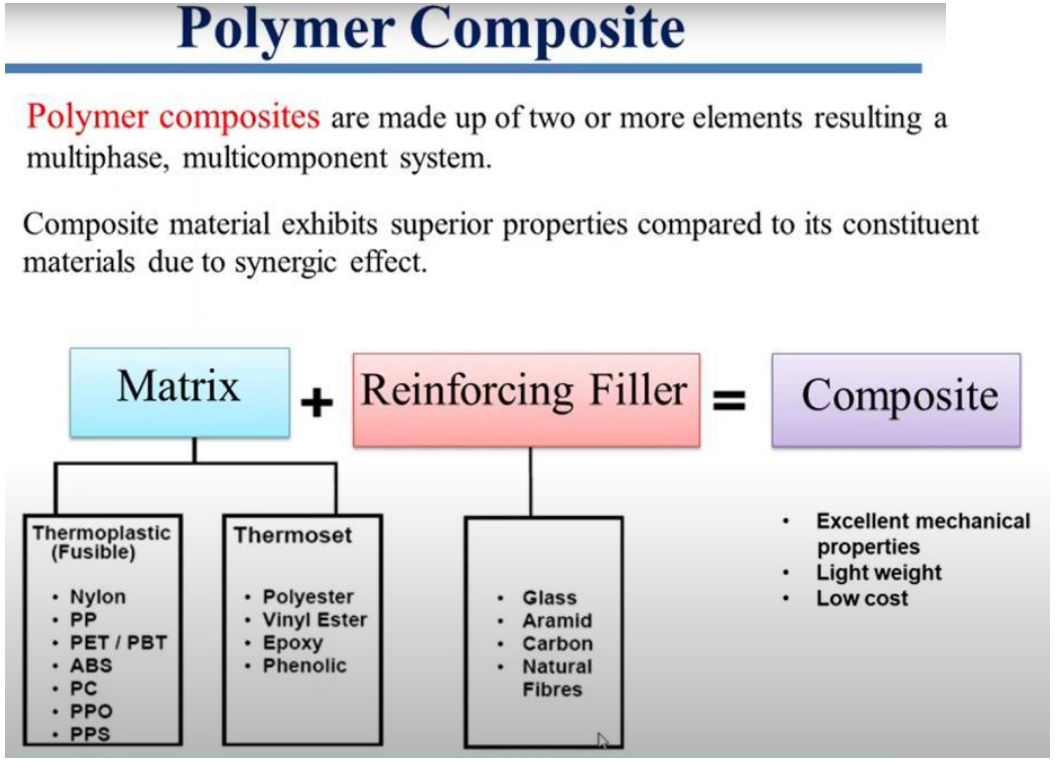
- These are made of metal (aluminum or titanium) and non-metal (oxides, nitride, or carbide).
- They are generally used for highly acidic or basic environments due to inertness.
- The disadvantage of ceramic membranes is the high sensitivity to temperature gradient, which leads to membrane cracking.



Zeolite membranes

- Zeolite membranes are suitable in highly-selective gas separation due to highly uniform pore size.
- It has a catalytic characteristic, which is beneficial for catalytic membrane reactor applications.
- Disadvantage of zeolite membranes include relatively low gas flux and thicker layer requirements to prevent cracks and pinholes.

Membrane material



Polymer Composite

Polymer composites are made up of two or more elements resulting a multiphase, multicomponent system.

Composite material exhibits superior properties compared to its constituent materials due to synergic effect.

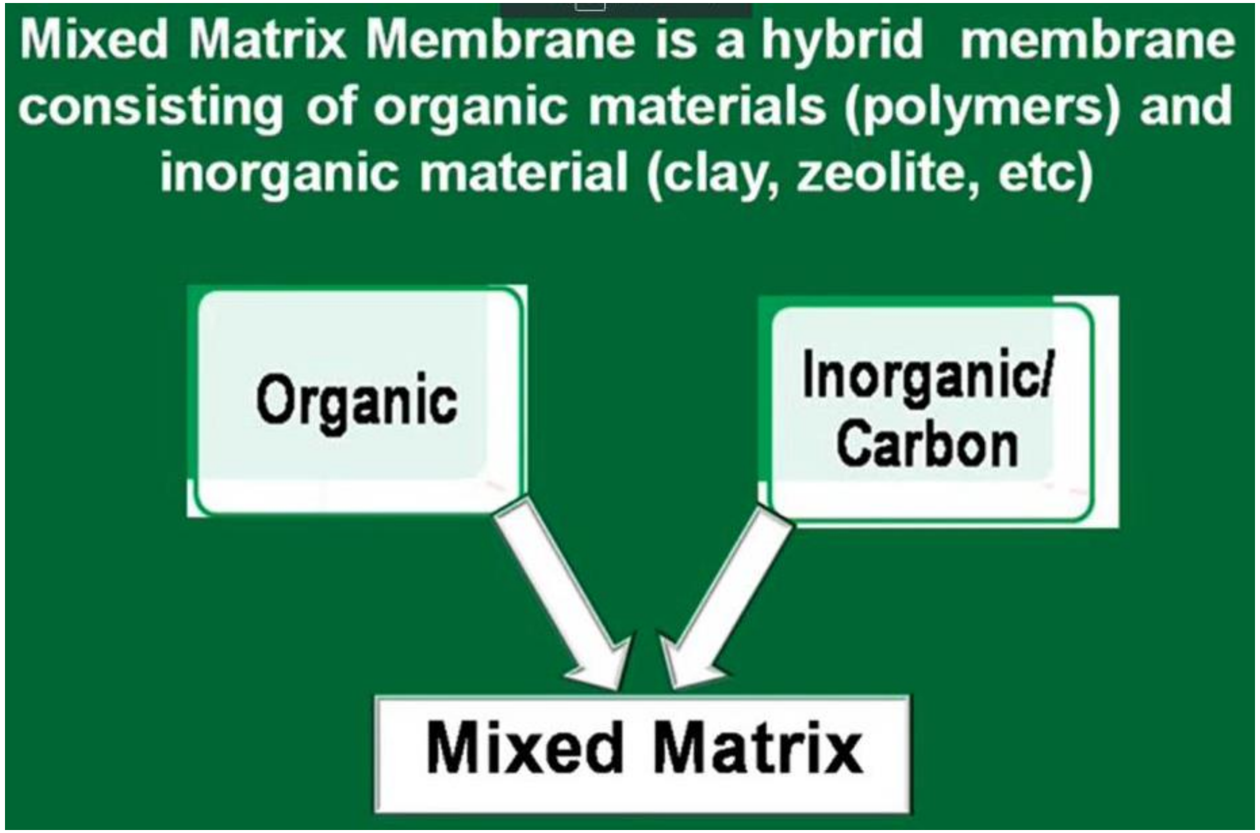
Matrix + Reinforcing Filler = Composite

Thermoplastic (Fusible)
- Nylon
- PP
- PET / PBT
- ABS
- PC
- PPO
- PPS

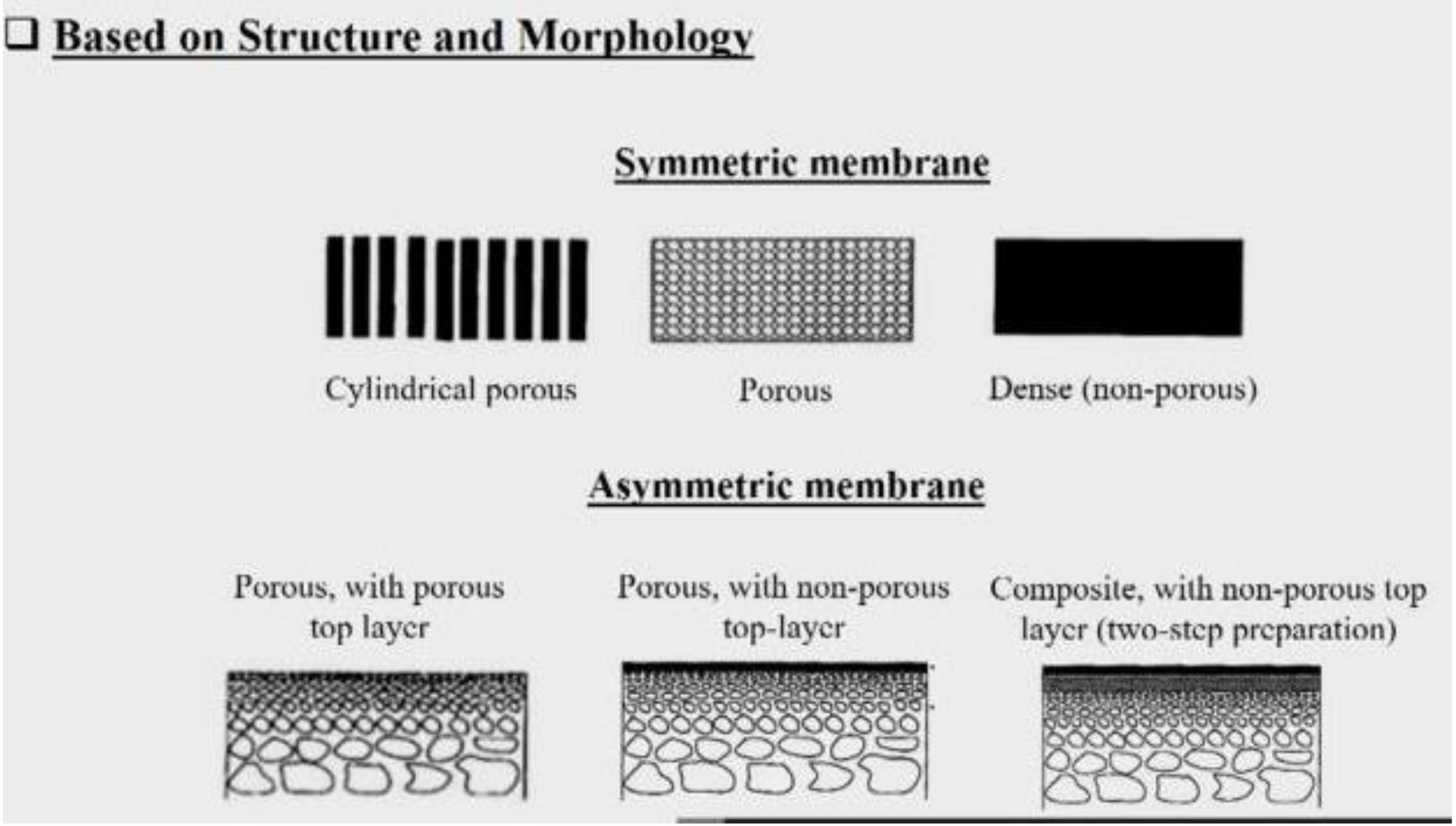
Thermoset
- Polyester
- Vinyl Ester
- Epoxy
- Phenolic

- Glass
- Aramid
- Carbon
- Natural Fibres

- Excellent mechanical properties
- Light weight
- Low cost



Mixed Matrix Membrane is a hybrid membrane consisting of organic materials (polymers) and inorganic material (clay, zeolite, etc)



❑ Based on Structure and Morphology

Symmetric membrane

Cylindrical porous

Porous

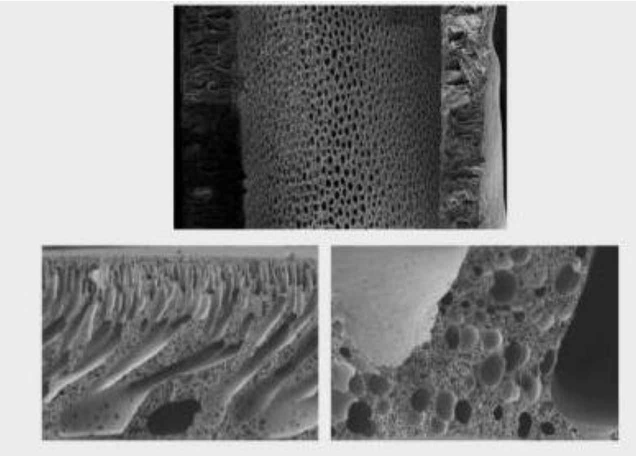
Dense (non-porous)

Asymmetric membrane

Porous, with porous top layer

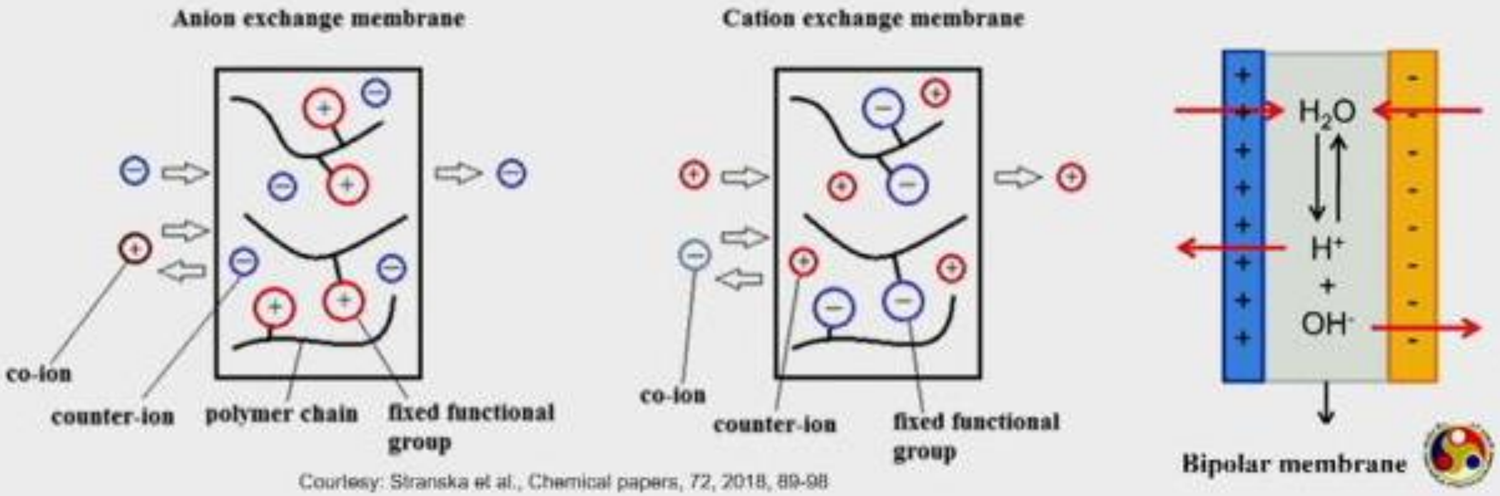
Porous, with non-porous top-layer

Composite, with non-porous top layer (two-step preparation)



❑ Based on Charges

Anion exchange membrane	Membrane containing fixed cationic charges and mobile anions that can be exchanged with other anions present in an external fluid in contact with membrane.
Cation exchange membrane	Membranes containing fixed anionic charges and mobile cations which can be exchanged with other cations present in an external fluid in contact with the membrane.
Bipolar membrane	Synthetic membrane containing two oppositely charged ion-exchanging layers in contact with each other.



Courtesy: Stranska et al., Chemical papers, 72, 2018, 89-98

Courtesy: Bunani et al., Desalination, 424, 2017, 37-44.

How are membranes designed in actual?

Module (device design):
Flat-Sheet vs Tubular

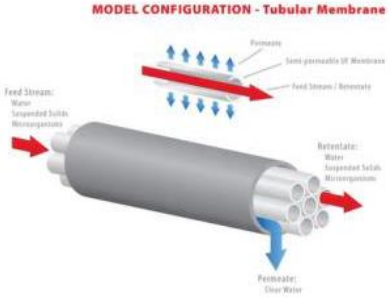
- desirable fluid dynamics
- cross-flow

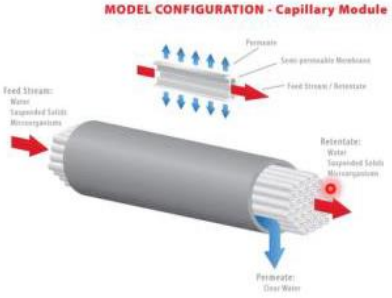
Credit: burkert.com

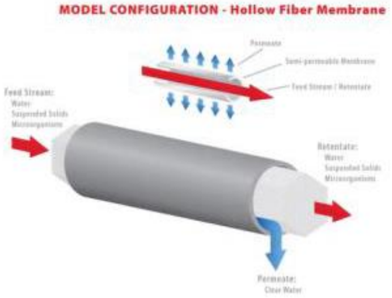
Tubular Membrane Modules

tubular, capillary, hollow-fiber

- increasing in number of tubes
- decreasing in tube size (L→R)



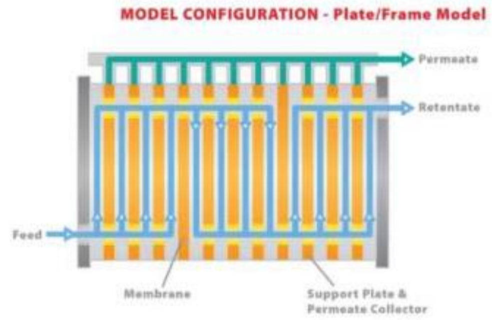




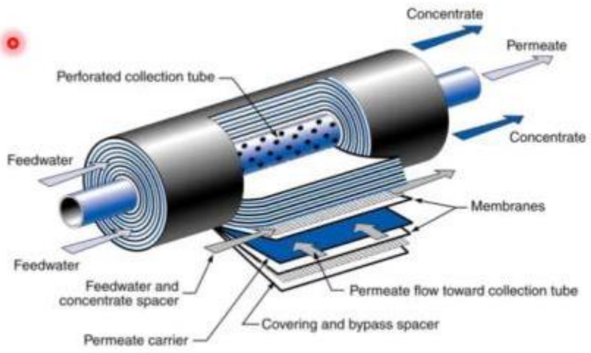
Flat-sheet Membrane Modules

plate-and-frame, spiral-wound

- increasing in compactness
- decreasing in versatility (L→R)



Credit: synderfiltration.com



Credit: chemdocwater.com

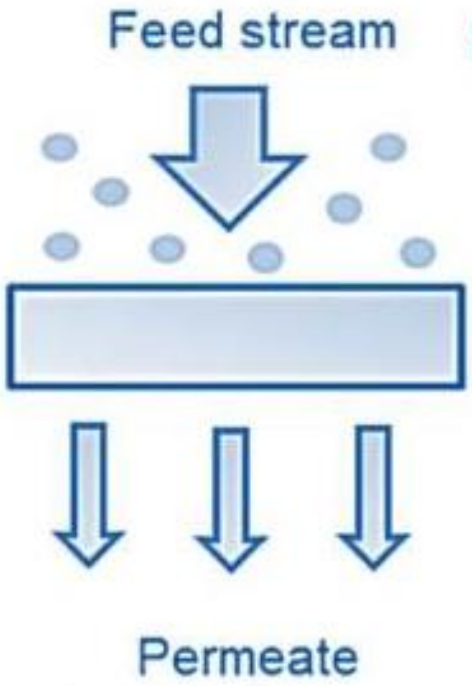
Module Configurations

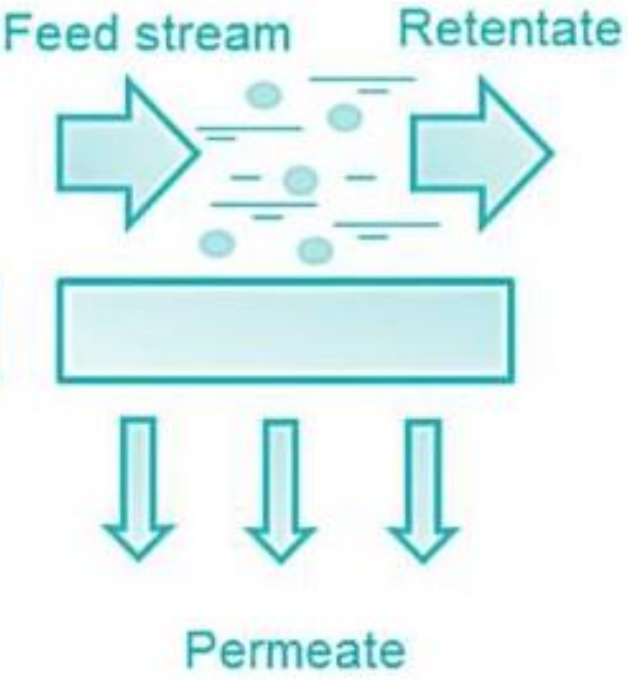
- **Different configurations of membranes are:**
  - Capillary Filtration
  - Cross Flow Membrane Operations
  - Hollow Fiber Membranes
  - Plate and Frame Membranes
  - Spiral Wound Membranes
  - Tubular membranes

Modes of Operation

Dead-end vs Cross-flow

normal flow vs tangential flow

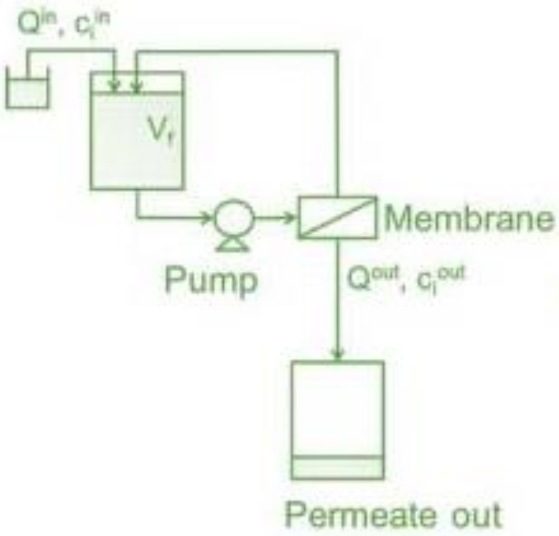




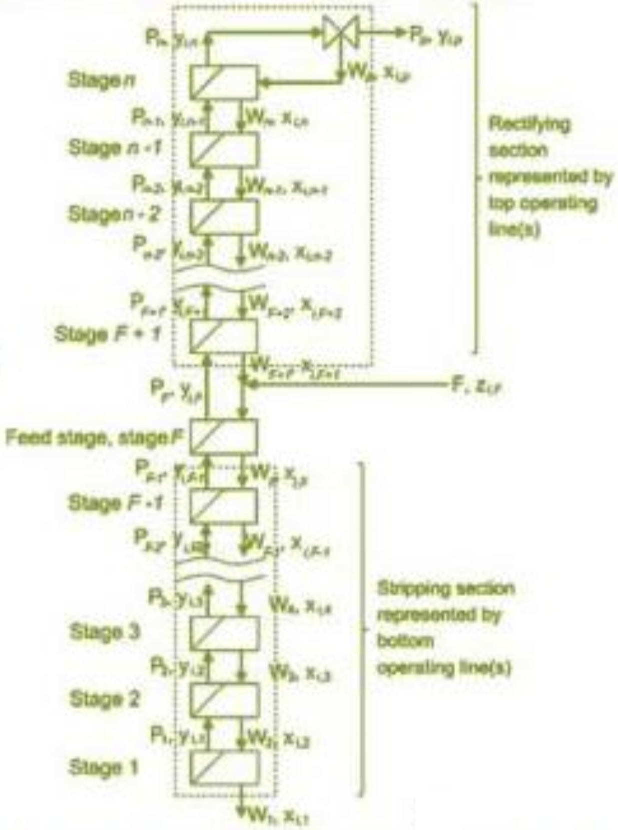
Credit: Baker (2000)

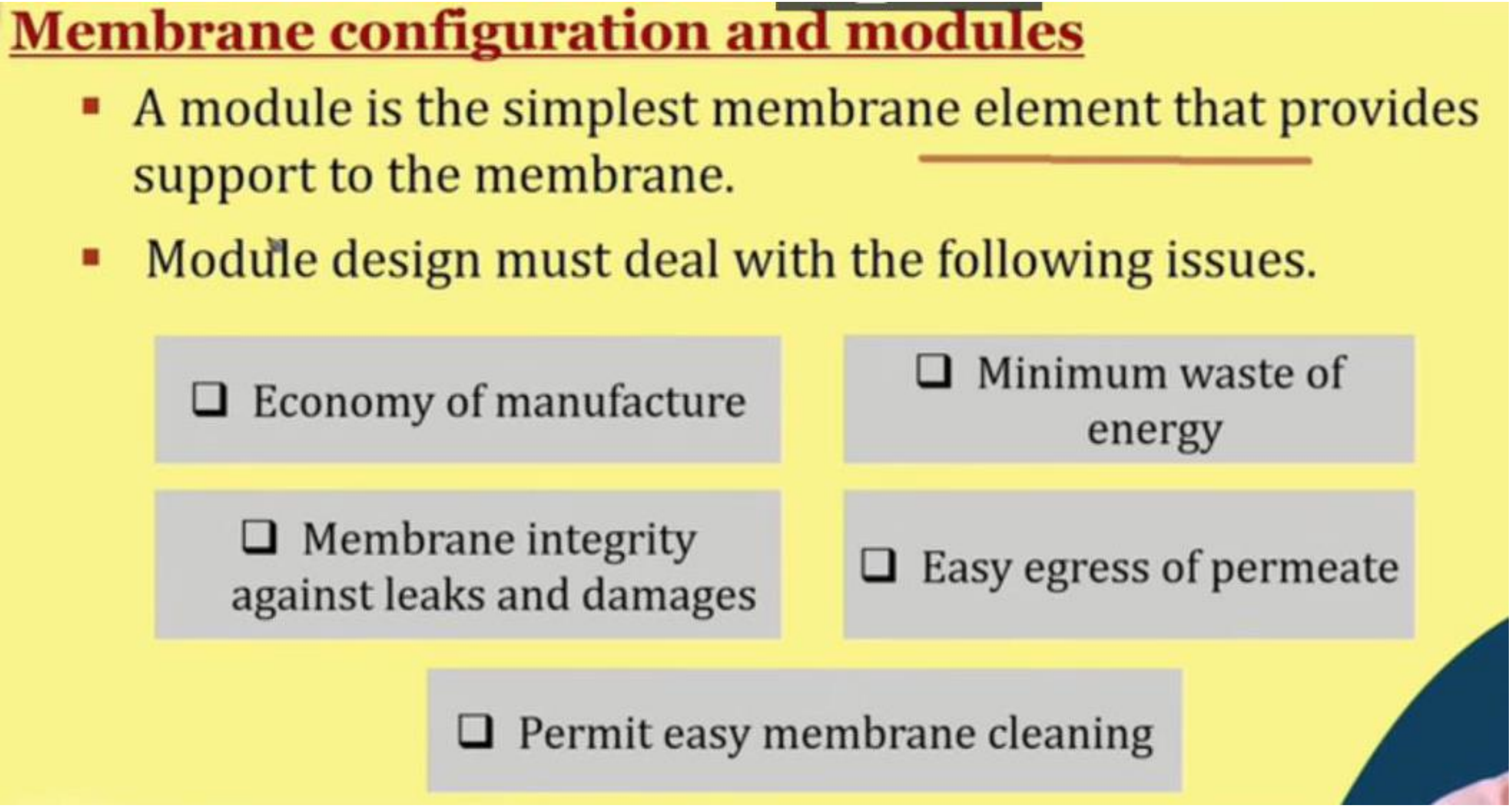
Batch vs Continuous

diafiltration vs membrane cascade



Credit: doi:10.1021/cr500006j





Membrane configuration and modules

- A module is the simplest membrane element that provides support to the membrane.
- Module design must deal with the following issues.

☐ Economy of manufacture

☐ Minimum waste of energy

☐ Membrane integrity against leaks and damages

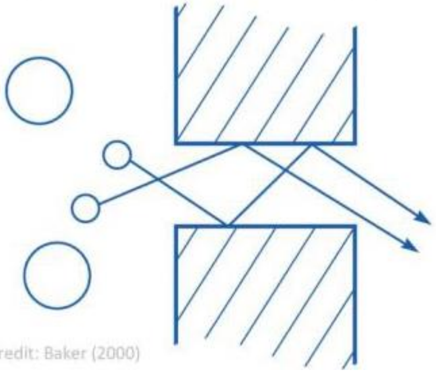
☐ Easy egress of permeate

☐ Permit easy membrane cleaning

How can we understand its transport?

Pore-flow model

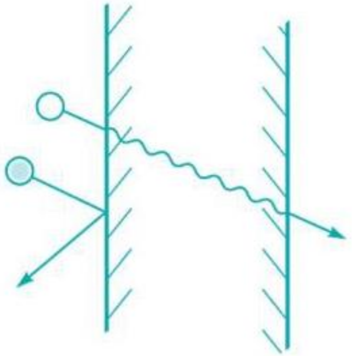
- for porous membranes
- pores ≈ cylindrical pipes



Credit: Baker (2000)

Solution-diffusion model

- for dense membranes
- 3 steps: sorption-diffusion-desorption



Basic membrane transport theories

Pore-flow model

- Darcy's law
- viscous convection
- DF: pressure gradient

$$J_{CV} = \frac{K'}{\mu}\boxed{\frac{dp}{dx}}$$

Solution-diffusion model

- Fick's law
- molecular diffusion
- DF: concentration gradient

$$J_{MD} = -D\boxed{\frac{dc}{dx}}$$

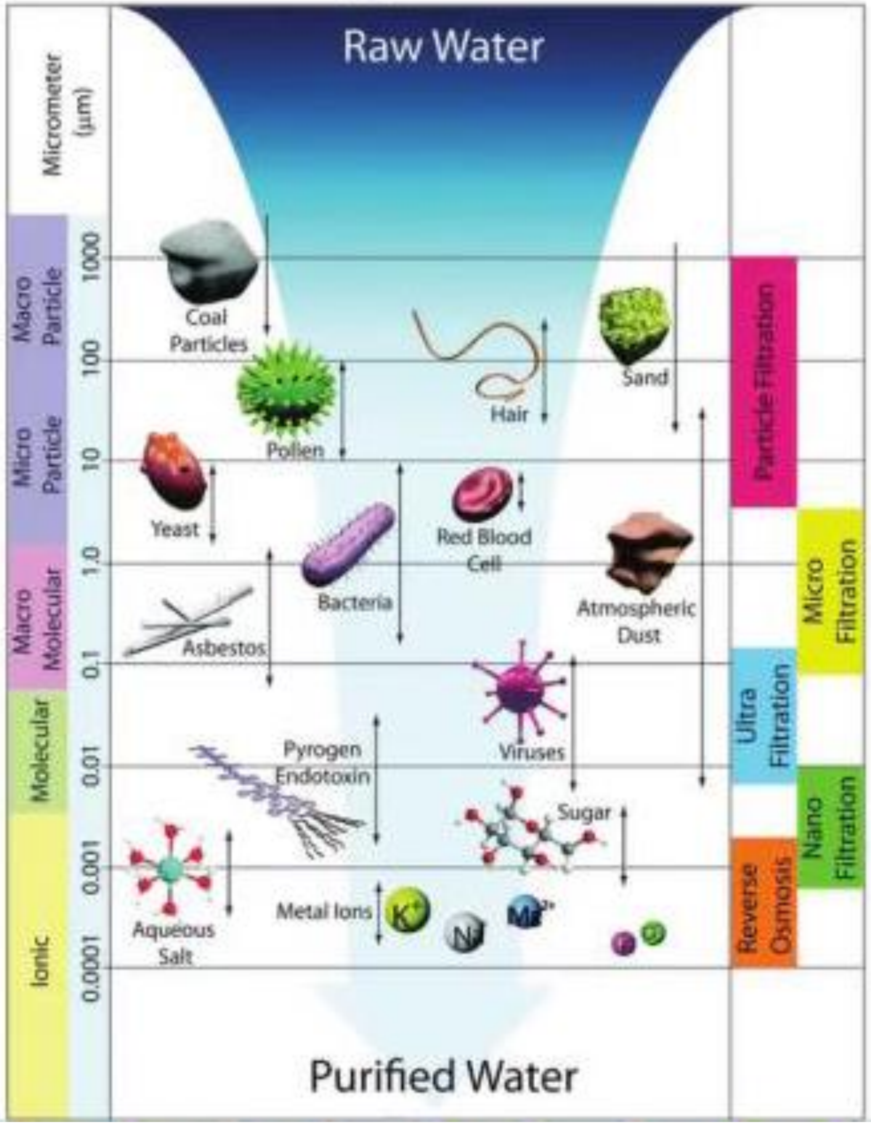
What are the pressure-driven processes?

1. Microfiltration (MF)
2. Ultrafiltration (UF)
3. Nanofiltration (NF)
4. Reverse Osmosis (RO)

porous membranes (MF, UF)

dense membranes (RO)

both type (NF)



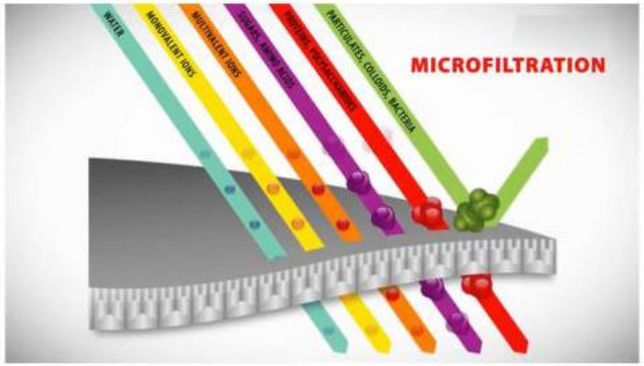
Credit: doi:10.5772/intechopen.69462

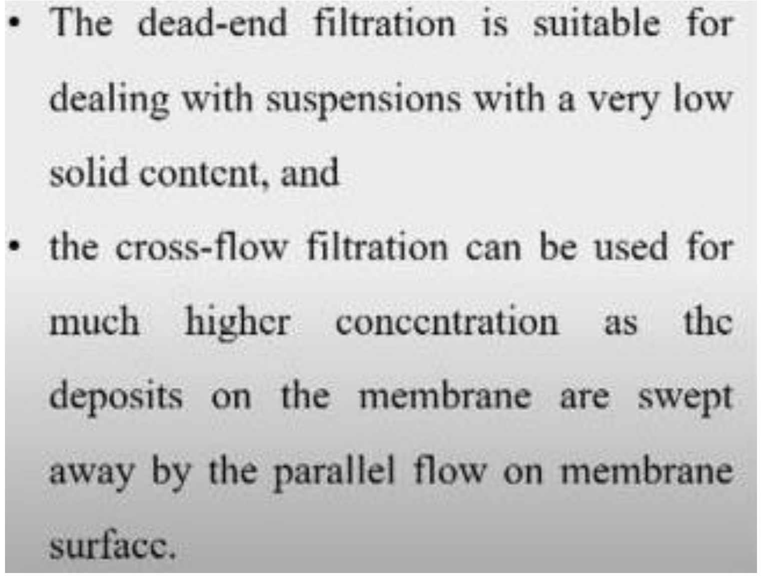
Microfiltration (MF)

size: 0.1 to 10 microns

particulates, colloids, bacteria

Applications: sterile filtration, process water pretreatment, wastewater treatment





- The dead-end filtration is suitable for dealing with suspensions with a very low solid content, and
- the cross-flow filtration can be used for much higher concentration as the deposits on the membrane are swept away by the parallel flow on membrane surface.

Ultrafiltration (UF)

size: 0.01 to 1 micron

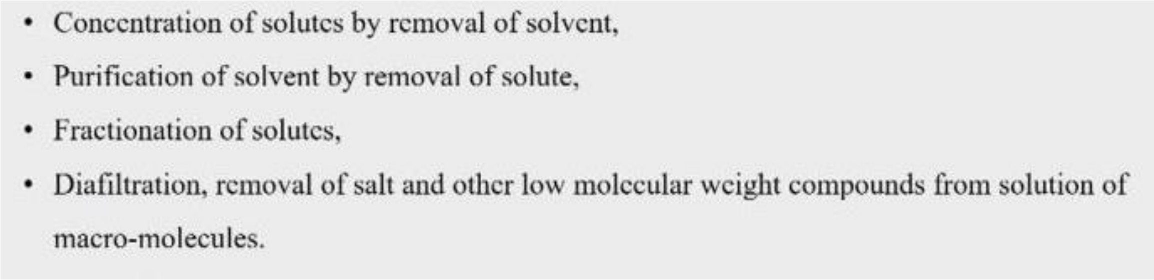
MW: 10^3 to 10^6 Dalton

proteins, polysaccharides

Applications: juice clarification, whey concentration [dairy], protein diafiltration [biotech], resource recovery & recycling [oils, paint], water reuse, water treatment

Credit: synderfiltration.com

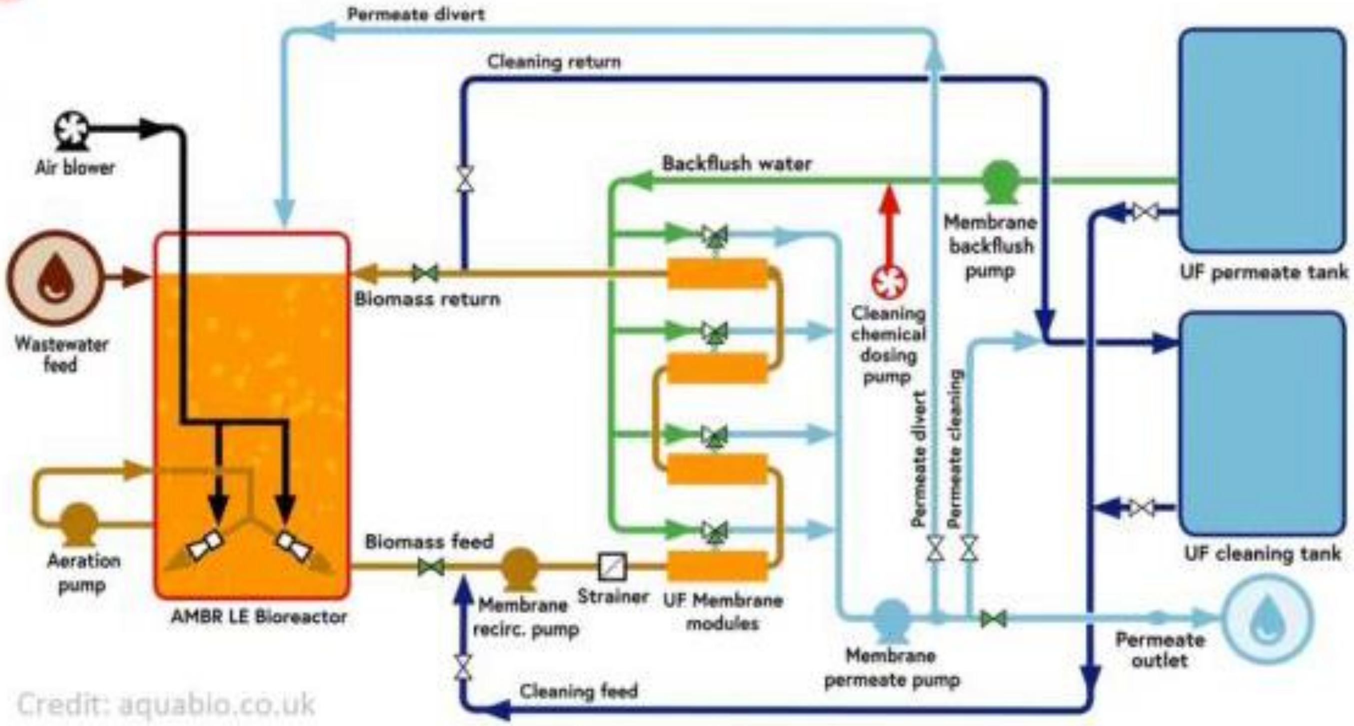
UF digunakan untuk :



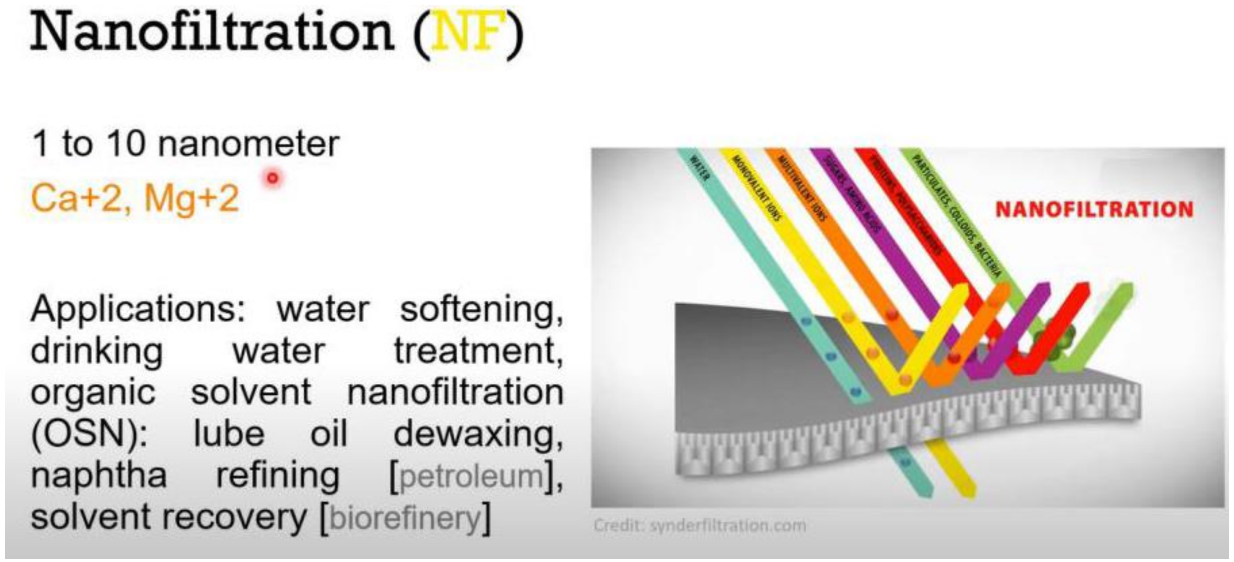
- Concentration of solutes by removal of solvent,
- Purification of solvent by removal of solute,
- Fractionation of solutes,
- Diafiltration, removal of salt and other low molecular weight compounds from solution of macro-molecules.

Membrane Bioreactor (MBR)

submerged (or external) MF/UF membranes in the activated sludge process (treatment + separation)



Credit: aquabio.co.uk



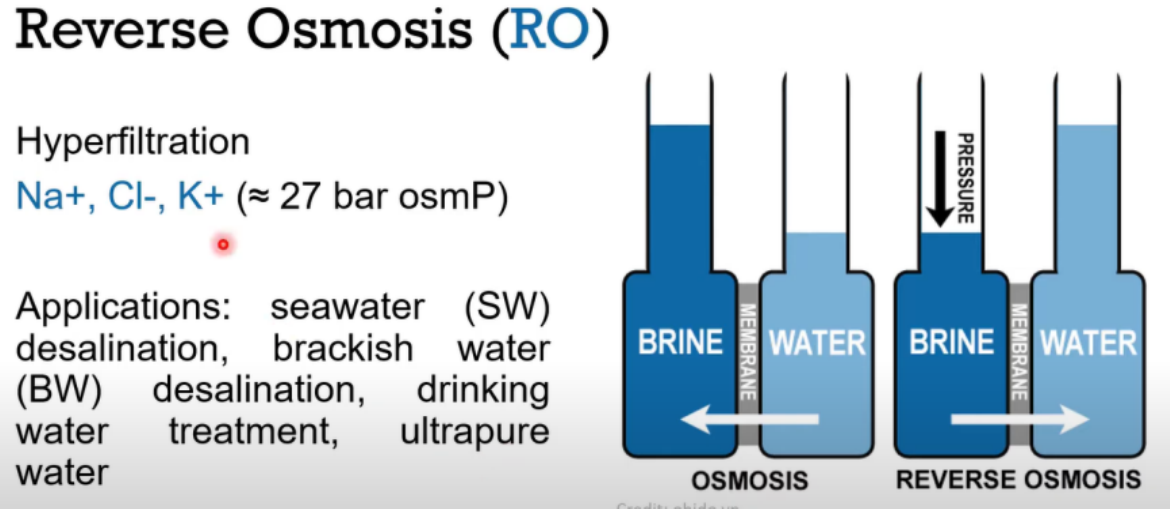
Nanofiltration (NF)

1 to 10 nanometer

Ca+2, Mg+2

Applications: water softening, drinking water treatment, organic solvent nanofiltration (OSN): lube oil dewaxing, naphtha refining [petroleum], solvent recovery [biorefinery]

Credit: synderfiltration.com



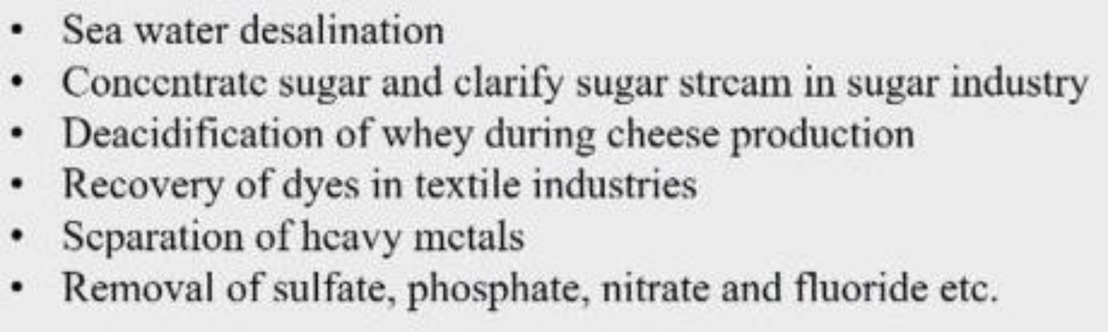
Reverse Osmosis (RO)

Hyperfiltration

Na+, Cl-, K+ (≈ 27 bar osmP)

Applications: seawater (SW) desalination, brackish water (BW) desalination, drinking water treatment, ultrapure water

NF digunakan untuk :

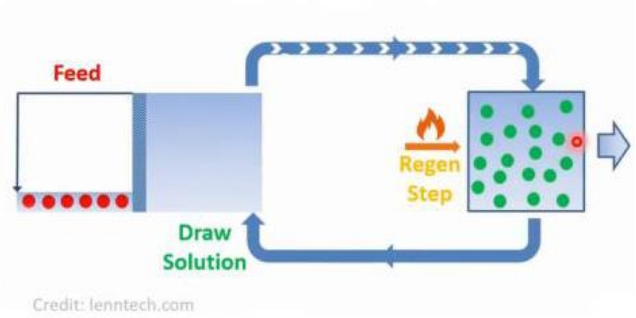


- Sea water desalination
- Concentrate sugar and clarify sugar stream in sugar industry
- Deacidification of whey during cheese production
- Recovery of dyes in textile industries
- Separation of heavy metals
- Removal of sulfate, phosphate, nitrate and fluoride etc.

Forward Osmosis (FO)

employs a draw solution (of high concentration) to induce water flow + regeneration step

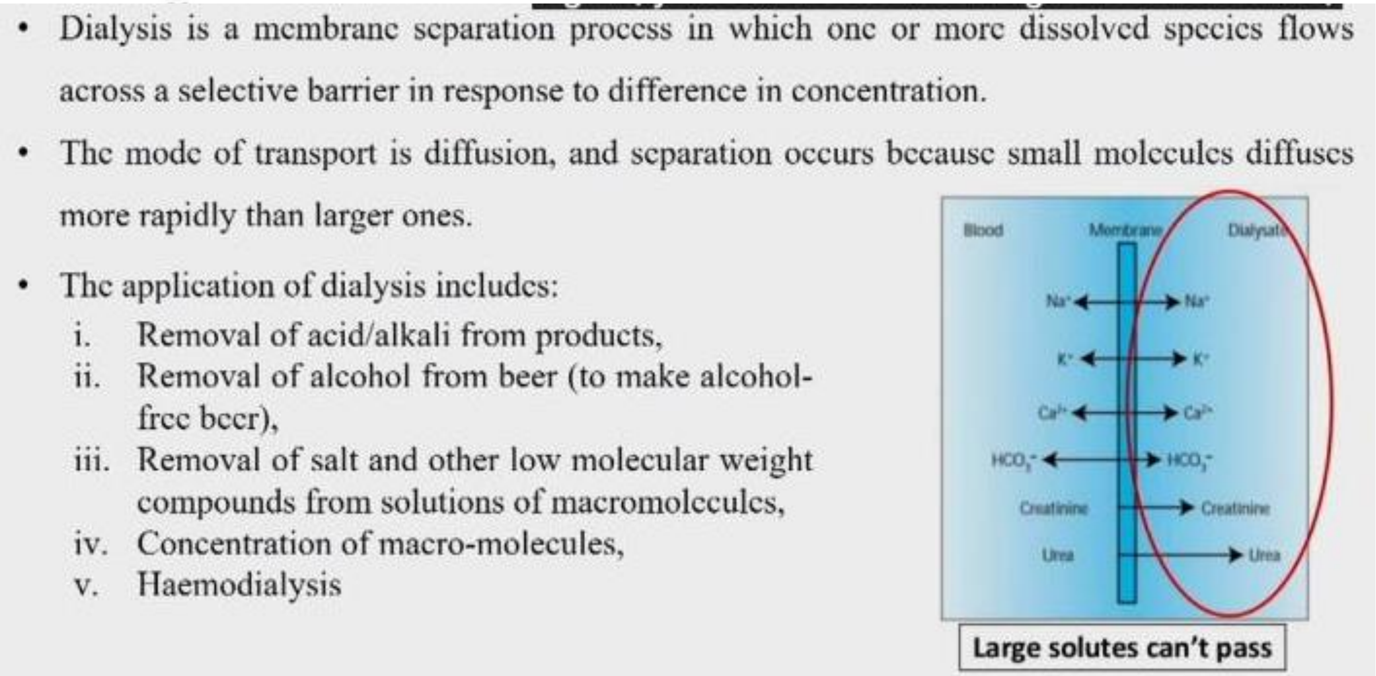
- Osmotic evaporation (OE)
- Membrane crystallization
  controlled hi-precision crystals



Credit: lenntech.com

Applications: waste volume reduction, FO/SWRO hybrid, concentration of heat-sensitive products [dairy, food, pharma]

Dialysis



- Dialysis is a membrane separation process in which one or more dissolved species flows across a selective barrier in response to difference in concentration.
- The mode of transport is diffusion, and separation occurs because small molecules diffuses more rapidly than larger ones.
- The application of dialysis includes:
  i. Removal of acid/alkali from products,
  ii. Removal of alcohol from beer (to make alcohol-free beer),
  iii. Removal of salt and other low molecular weight compounds from solutions of macromolecules,
  iv. Concentration of macro-molecules,
  v. Haemodialysis

Large solutes can't pass

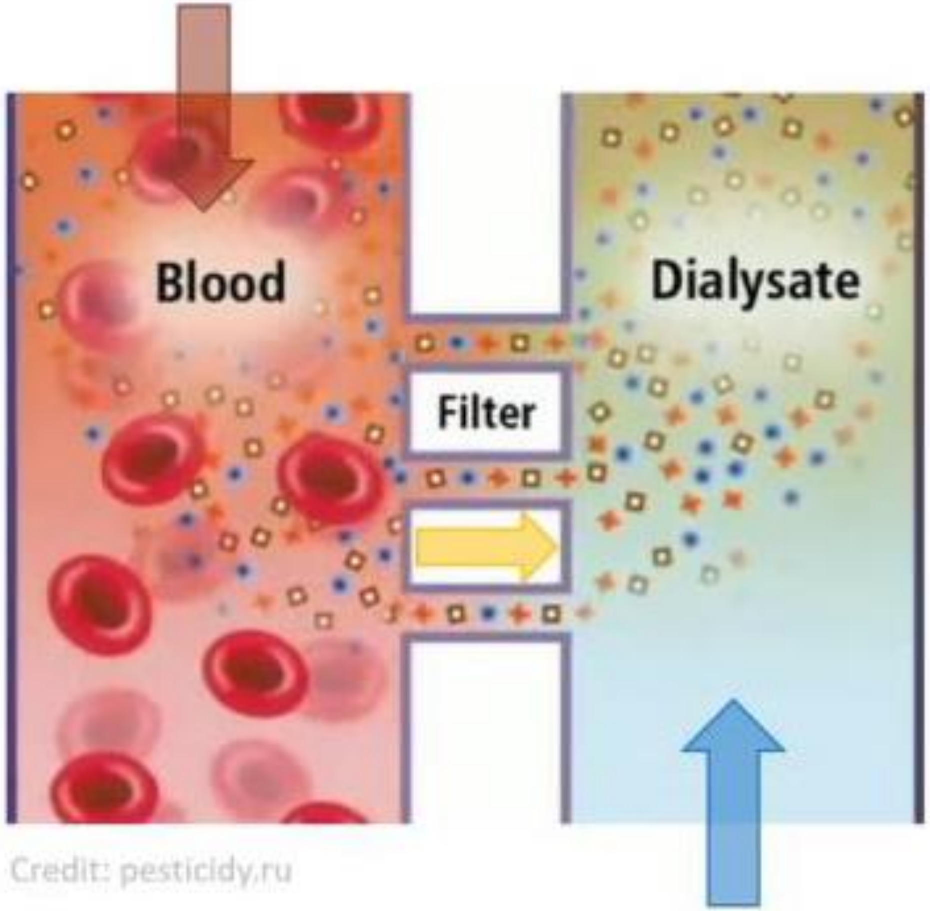
Membranes in Regenerative Medicine

a) Hemodialysis (artificial kidney)

b) Membrane blood oxygenator (MBO) (artificial lungs)

c) Bio-artificial pancreas (BAP)

d) Tissue scaffolds for tissue engineering (stem cells into organs for transplant)

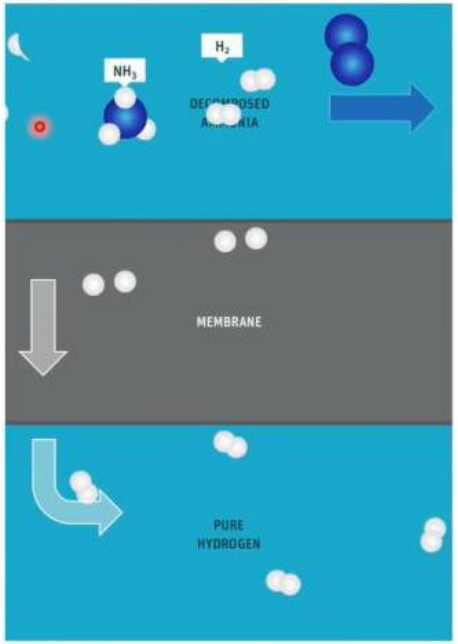


Credit: pesticidy.ru

Gas Separation (GS)

allows separation of gases based on their molecular weight and/or their affinity to membrane material

Applications: carbon capture, gas scrubbing (*SOx, NOx, CO2*) [flue gas], gas sweetening (*H2S, CO2*) & dehydration [petroleum], N2/O2 enrichment, hydrogen production from ammonia (*H2*)

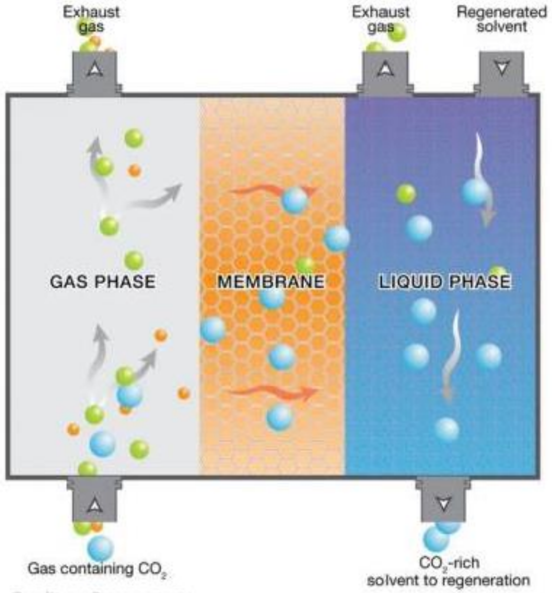


Gas-Liquid Membrane Contactor

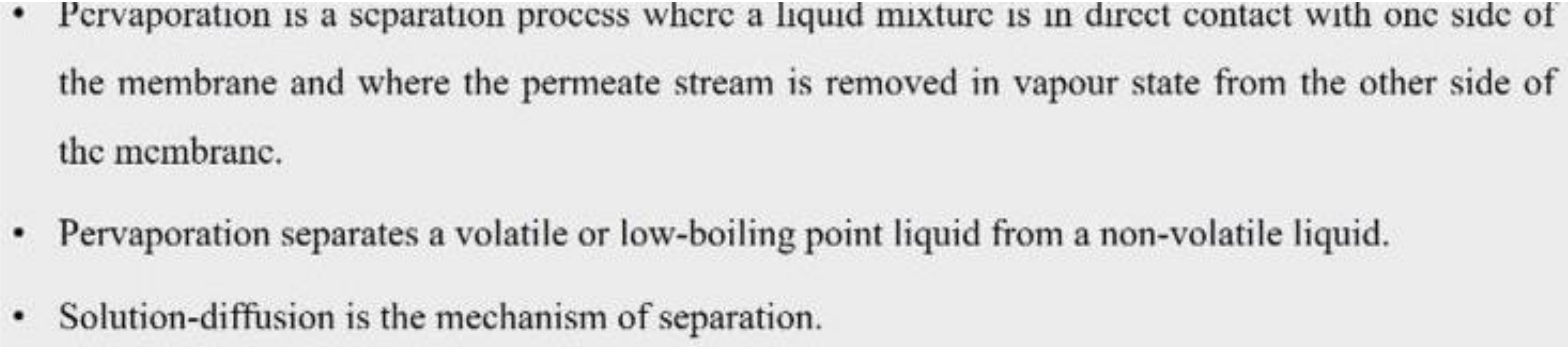
Gas absorption/stripping

allows for simultaneous degassing and bubbling

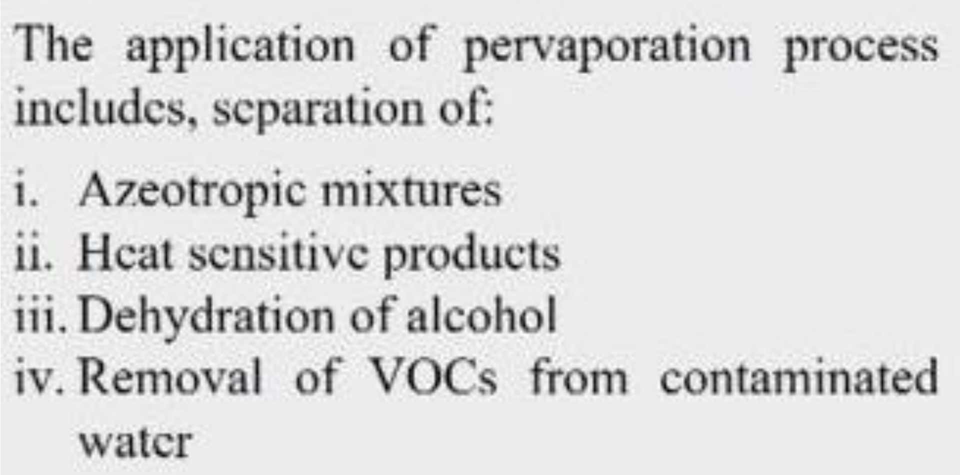
Applications: gas addition/removal (*O2, CO2, N2*) [beverage], water deaeration [utilities], ammonia stripping [wastewater], carbon capture [flue gas], gas sweetening (*CO2, H2S*) & dehydration [petroleum]



Pervaporation (PV)

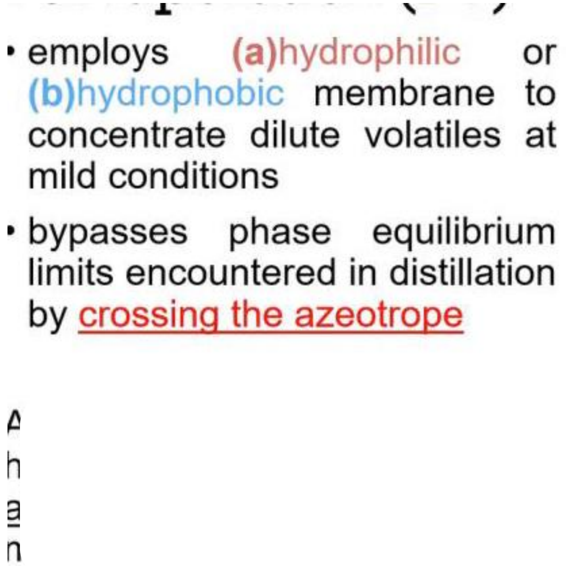


- Pervaporation is a separation process where a liquid mixture is in direct contact with one side of the membrane and where the permeate stream is removed in vapour state from the other side of the membrane.
- Pervaporation separates a volatile or low-boiling point liquid from a non-volatile liquid.
- Solution-diffusion is the mechanism of separation.



The application of pervaporation process includes, separation of:

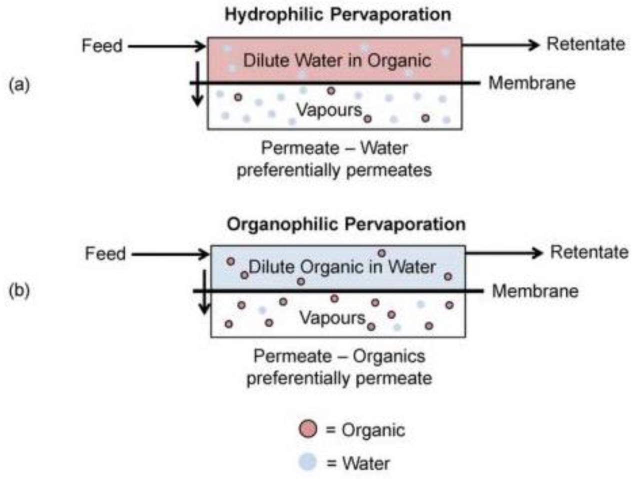
i. Azeotropic mixtures
ii. Heat sensitive products
iii. Dehydration of alcohol
iv. Removal of VOCs from contaminated water



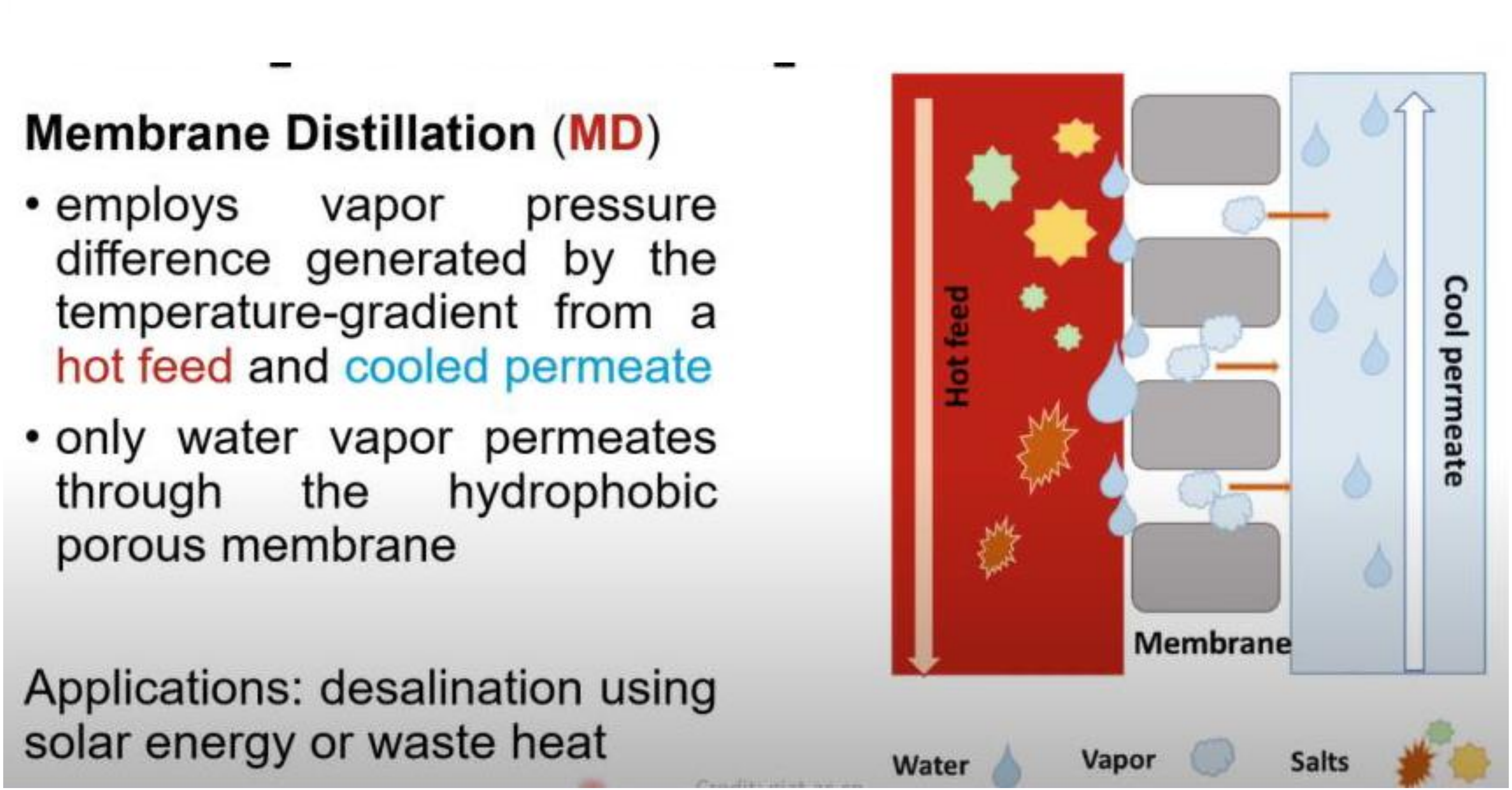
- employs **(a)**hydrophilic or **(b)**hydrophobic membrane to concentrate dilute volatiles at mild conditions
- bypasses phase equilibrium limits encountered in distillation by crossing the azeotrope

A
h
a
n

Credit: doi:10.3390/membranes6010017



vapor permeation (VP) if feed = gas phase



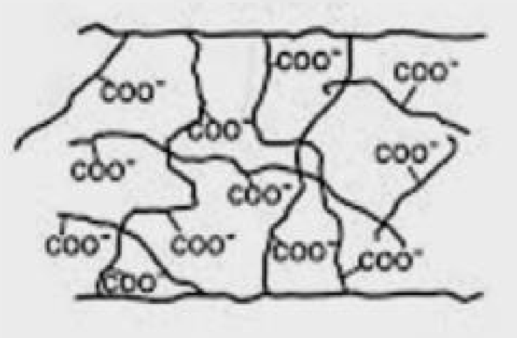
Membrane Distillation (MD)

- employs vapor pressure difference generated by the temperature-gradient from a hot feed and cooled permeate
- only water vapor permeates through the hydrophobic porous membrane

Applications: desalination using solar energy or waste heat

Electrically charged membranes

- The electrically charged membranes can be dense or microporous, but are most commonly very finely microporous, with the walls carrying fixed positive or negative charged ions.
- A membrane with fixed positively charged ions is referred as an anion exchange membrane because it binds anions in the surrounding fluid.
- A membrane containing fixed negatively charged ions are called cation exchange membranes.
- The separation with charged membranes is achieved mainly by the exclusion of ions of the same charge as the fixed ions of the membrane structure and to a much lesser extent by the pore size.
- Separation is affected by the charge and concentration of ions in the solution.



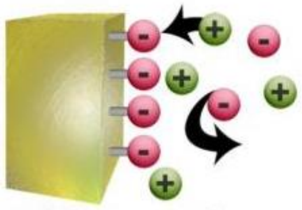
Electrically charged membrane

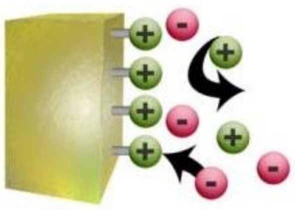
What are electro-membrane processes?

uses ion exchange membranes
(porous & dense):

cation exchange membranes (CEM)

anion exchange membranes (AEM)


CATION exchange matrix

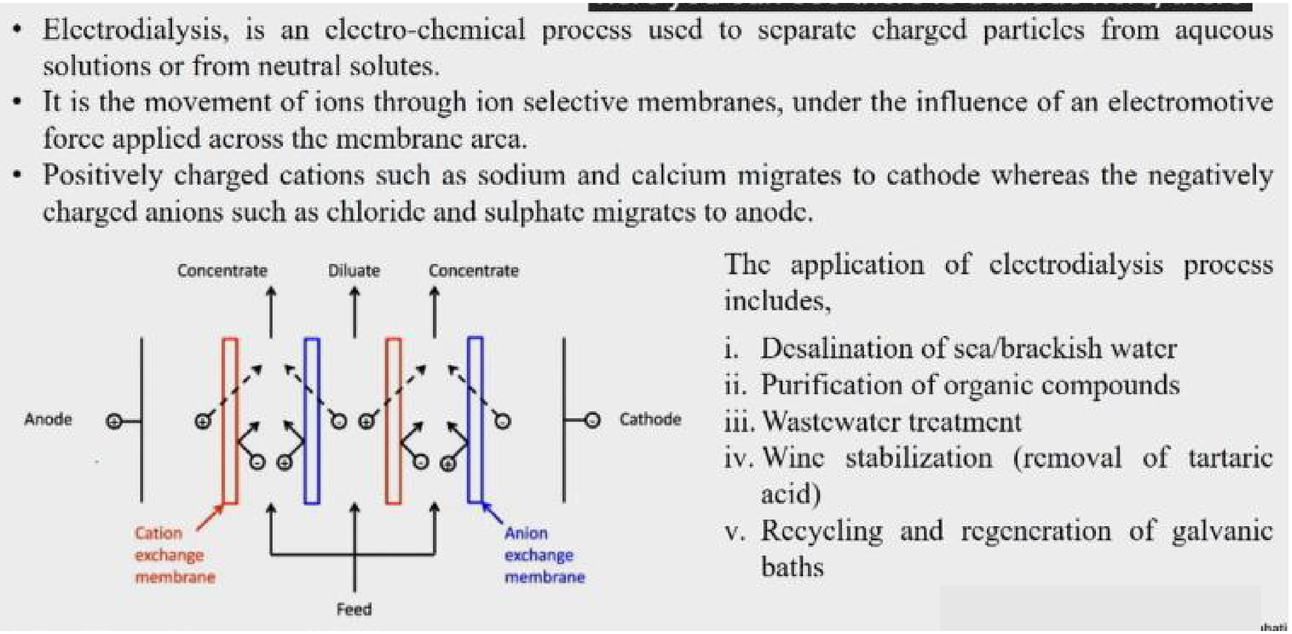

ANION exchange matrix

For chemical production:
- Membrane Electrolysis (ME)

For purification:
- Electrodialysis (ED)
- Donnan Dialysis (DD)

For power generation:
- Reverse Electrodialysis (RED)
- Fuel Cells (FC)

Electrodialysis (ED)



- Electrodialysis, is an electro-chemical process used to separate charged particles from aqueous solutions or from neutral solutes.
- It is the movement of ions through ion selective membranes, under the influence of an electromotive force applied across the membrane area.
- Positively charged cations such as sodium and calcium migrates to cathode whereas the negatively charged anions such as chloride and sulphate migrates to anode.

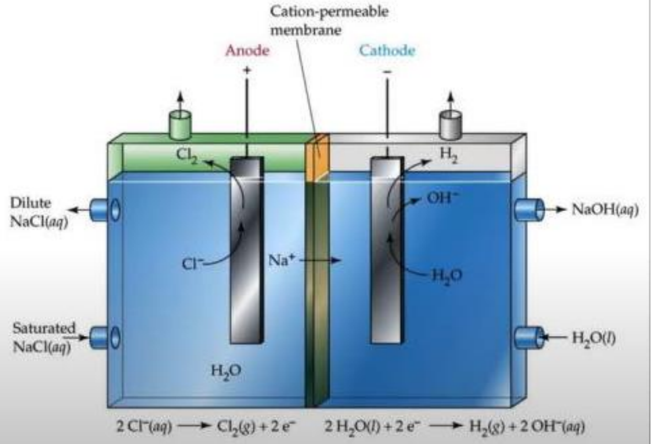
The application of electrodialysis process includes,

i. Desalination of sea/brackish water
ii. Purification of organic compounds
iii. Wastewater treatment
iv. Wine stabilization (removal of tartaric acid)
v. Recycling and regeneration of galvanic baths

Membrane Electrolysis (ME)

allows for simultaneous electrode reaction + separation of electrolysis products

Applications: chlor-alkali process (*brine → Cl2 + NaOH*), water electrolysis (*H2O → H2*) [energy], production of oxidative agents for water disinfection



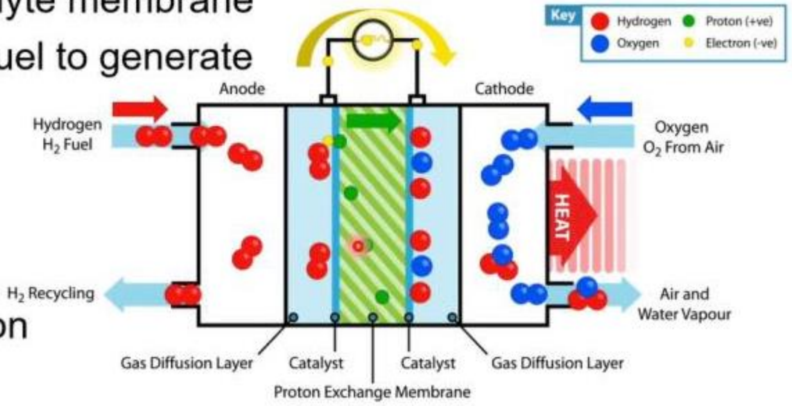
Fuel Cells (FC)

- specifically, PEM fuel cells
- PEM = polymer electrolyte membrane
- employs hydrogen as fuel to generate electricity

Applications:

FCs for transportation,

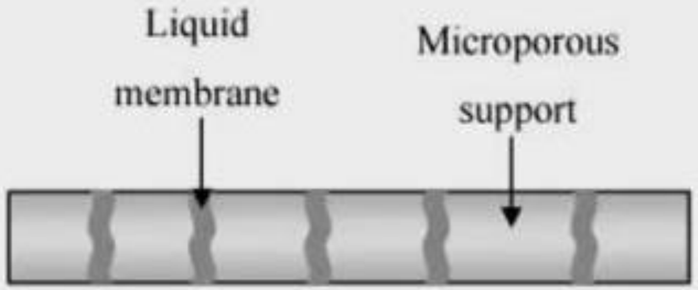
portable power generation



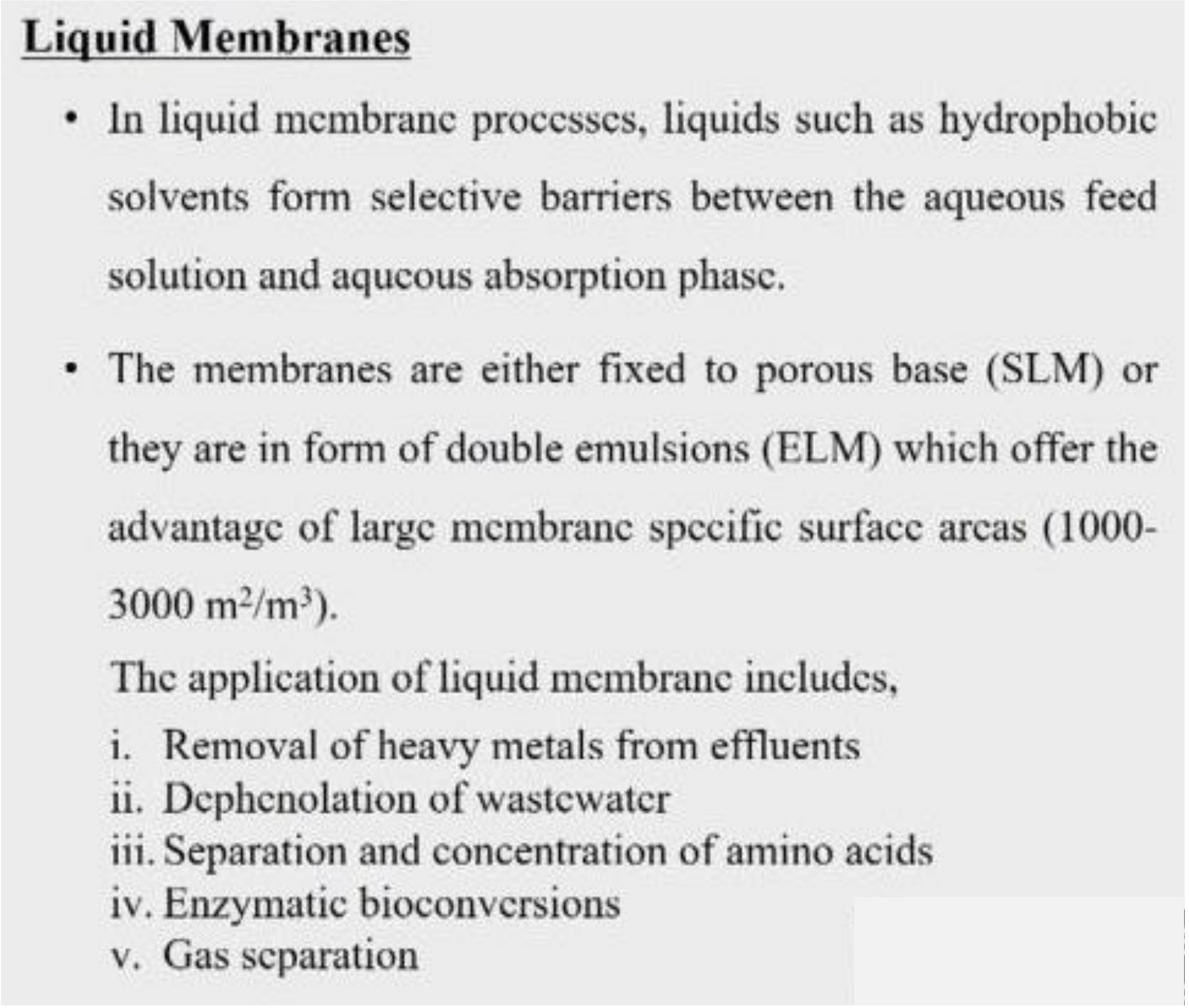
Credit: intelligent-energy.com

Liquid Membranes

- Liquid membranes have become increasingly significant in the context of facilitated transport, which utilizes "carriers" to selectively transport components such as metal ions at a relatively high rate across the membrane interface.
- Liquid membrane literally is a membrane made up of liquid.
- It consists of a liquid phase (e.g. a thin oil film) existing either in supported or unsupported form that serves as a membrane barrier between two phases of aqueous solutions or gas mixtures.
- Liquid membranes are used on a pilot-plant scale for selective removal of heavy-metal ions and organic solvents from industrial waste streams.
- They have also been used for the separation of oxygen and nitrogen.



Supported liquid membrane

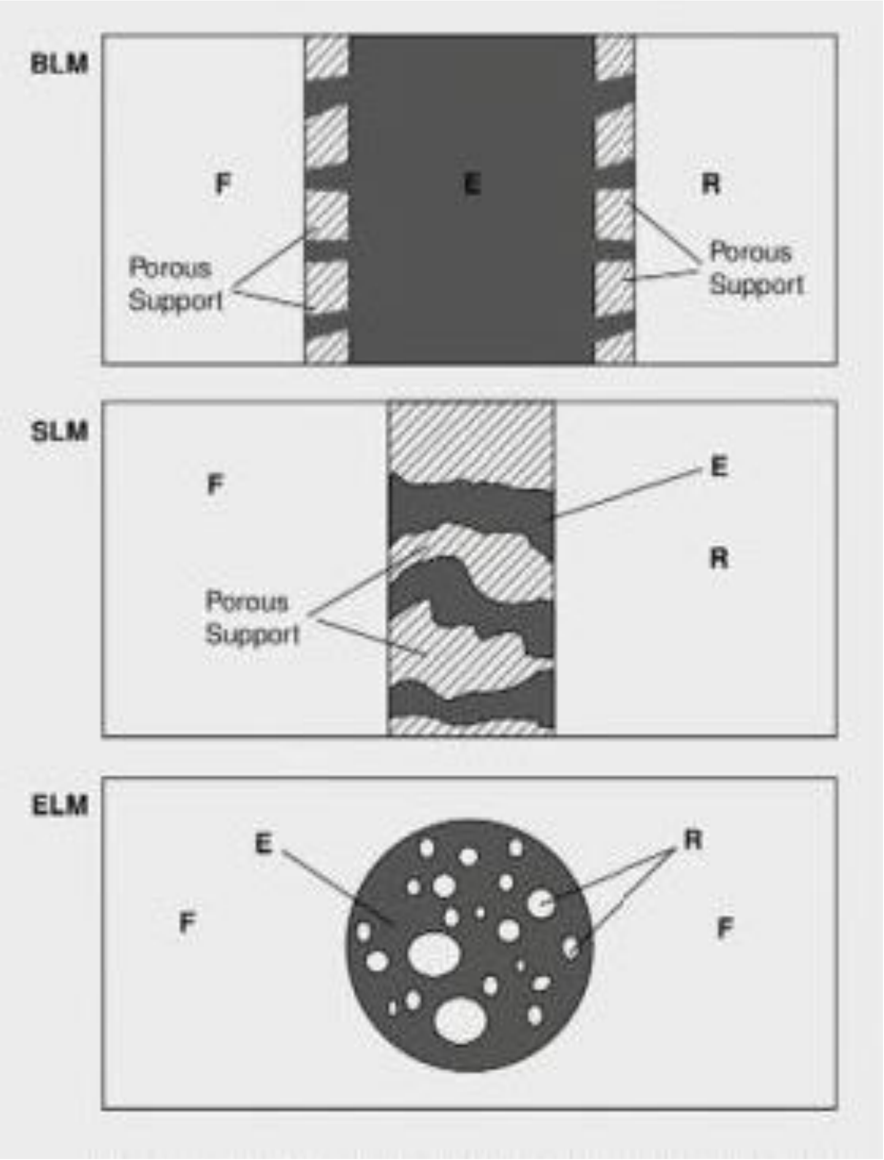


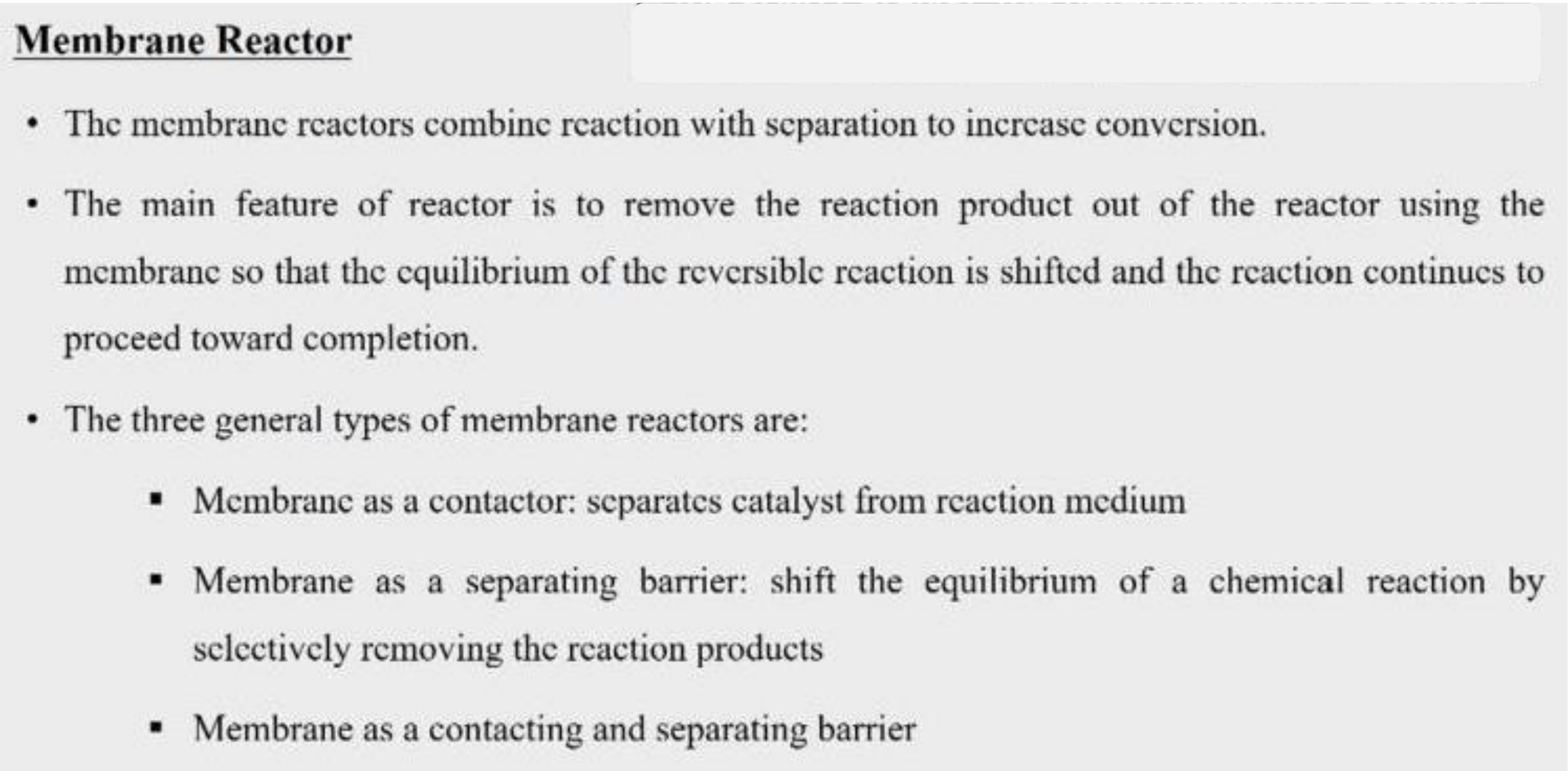
Liquid Membranes

- In liquid membrane processes, liquids such as hydrophobic solvents form selective barriers between the aqueous feed solution and aqueous absorption phase.
- The membranes are either fixed to porous base (SLM) or they are in form of double emulsions (ELM) which offer the advantage of large membrane specific surface areas (1000-3000 m^2/m^3).

The application of liquid membrane includes,

i. Removal of heavy metals from effluents
ii. Dephenolation of wastewater
iii. Separation and concentration of amino acids
iv. Enzymatic bioconversions
v. Gas separation

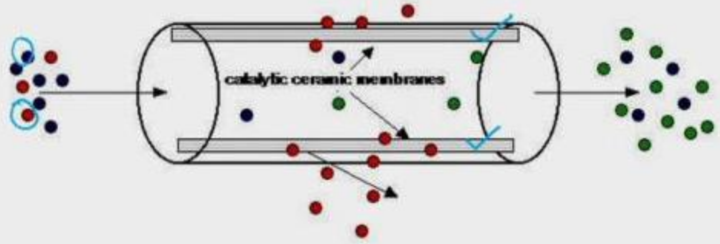




Membrane Reactor

- The membrane reactors combine reaction with separation to increase conversion.
- The main feature of reactor is to remove the reaction product out of the reactor using the membrane so that the equilibrium of the reversible reaction is shifted and the reaction continues to proceed toward completion.
- The three general types of membrane reactors are:
    - Membrane as a contactor: separates catalyst from reaction medium
    - Membrane as a separating barrier: shift the equilibrium of a chemical reaction by selectively removing the reaction products
    - Membrane as a contacting and separating barrier

Membrane Reactor



A mixed feed of **A** and **B** enters the membrane reactor. **C** is produced in the reactor, and **B** diffuses out through the membrane pores.


Wastewater treatment

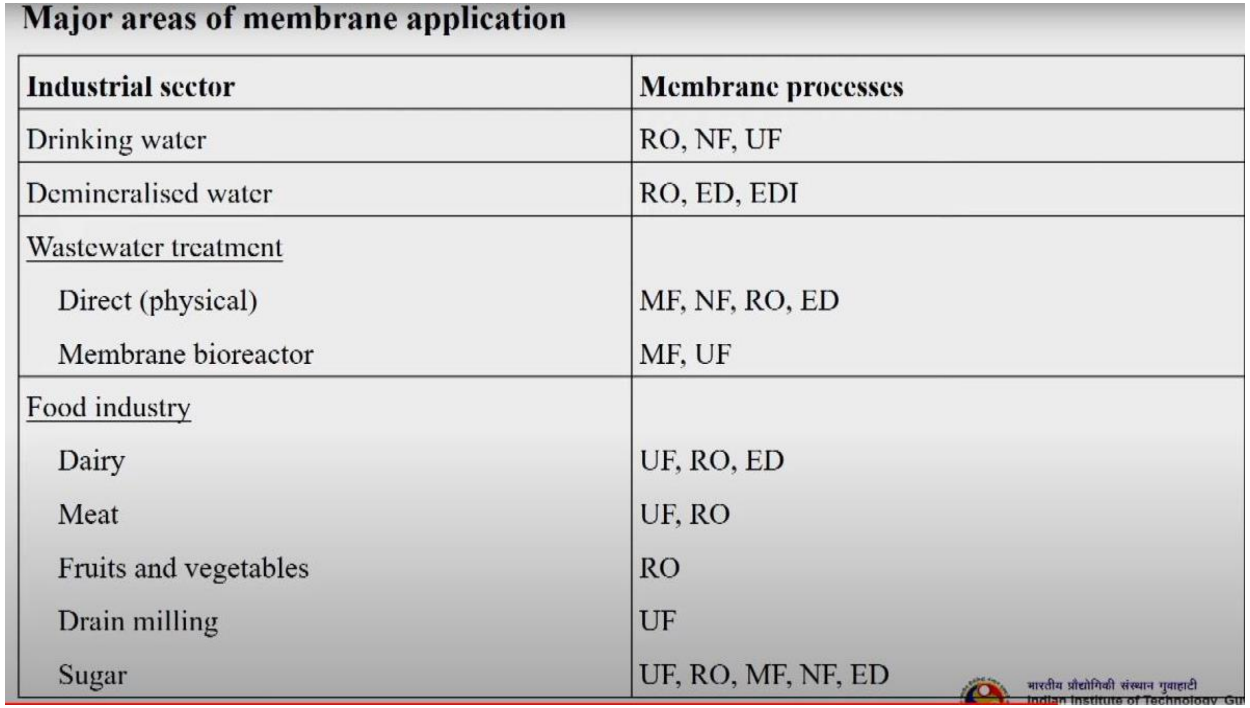
Food and beverages industries

Pharmaceuticals and Bio-technology

Chemical industries

Desalination

Applications of Membrane Technology


Major areas of membrane application

Industrial sector	Membrane processes
Drinking water	RO, NF, UF
Demineralised water	RO, ED, EDI
Wastewater treatment	
Direct (physical)	MF, NF, RO, ED
Membrane bioreactor	MF, UF
Food industry	
Dairy	UF, RO, ED
Meat	UF, RO
Fruits and vegetables	RO
Drain milling	UF
Sugar	UF, RO, MF, NF, ED

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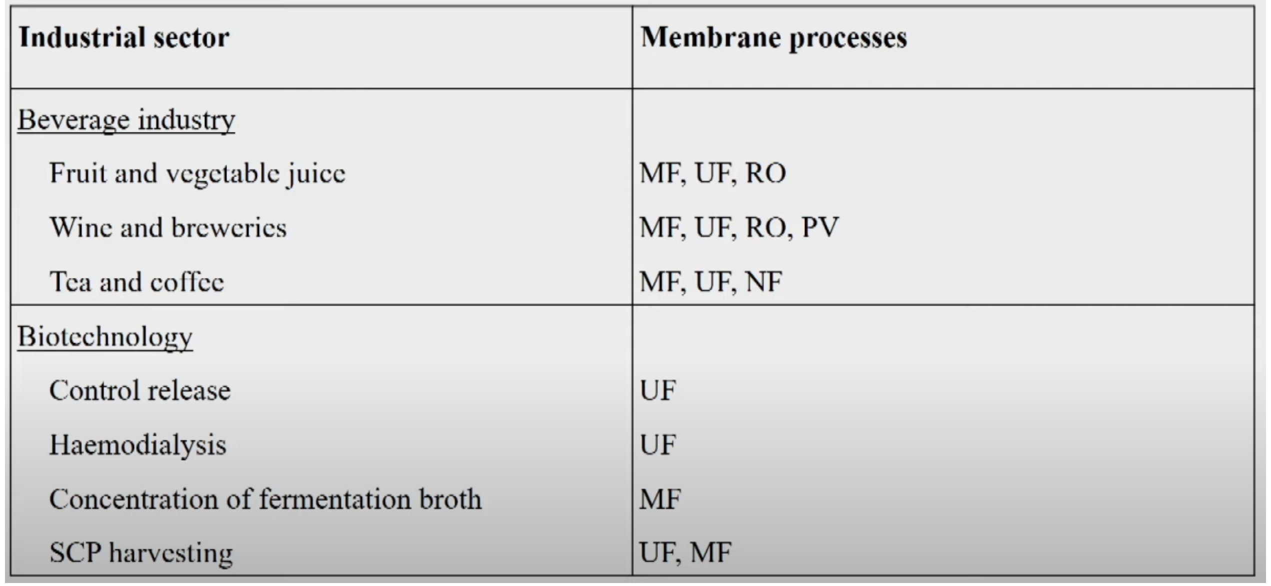
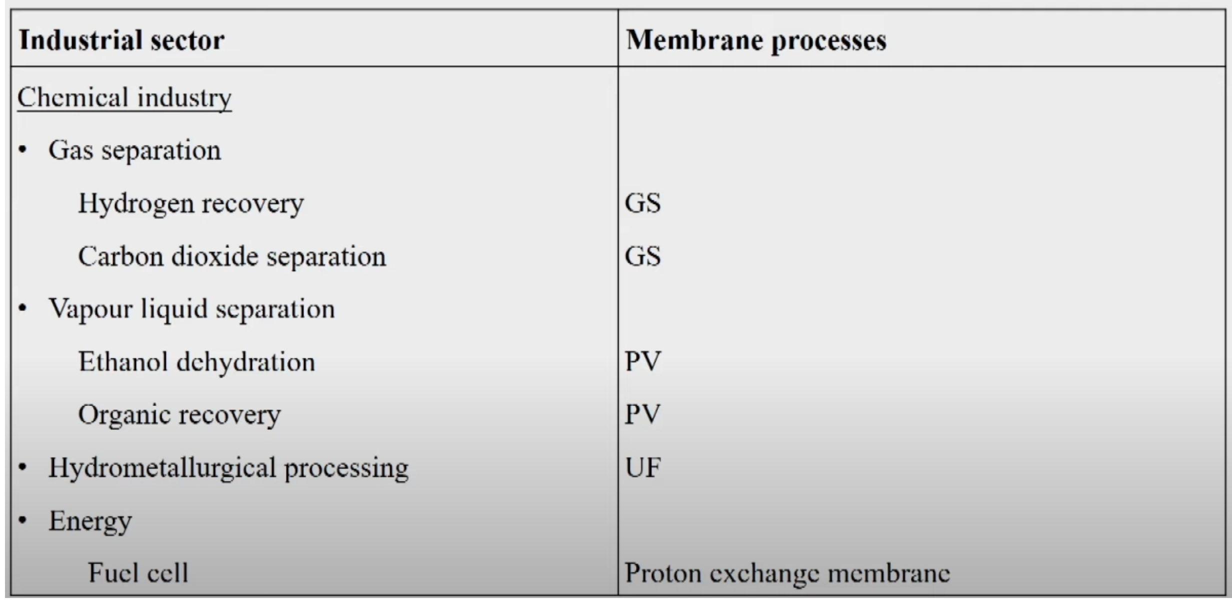
Indian Institute of Technology Gu

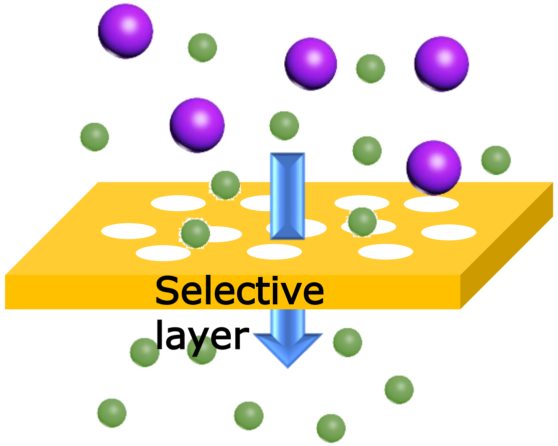

Industrial sector	Membrane processes
Beverage industry	
Fruit and vegetable juice	MF, UF, RO
Wine and breweries	MF, UF, RO, PV
Tea and coffee	MF, UF, NF
Biotechnology	
Control release	UF
Haemodialysis	UF
Concentration of fermentation broth	MF
SCP harvesting	UF, MF


Industrial sector	Membrane processes
Chemical industry	
• Gas separation	
Hydrogen recovery	GS
Carbon dioxide separation	GS
• Vapour liquid separation	
Ethanol dehydration	PV
Organic recovery	PV
• Hydrometallurgical processing	UF
• Energy	
Fuel cell	Proton exchange membrane

PROSES PEMISAHAN

Transport through the membrane

Oleh : Indah Prihatiningtyas D.S



Porous and Non-porous Membranes

- Membranes can be classified in two main groups: (i) Porous and (ii) non-porous

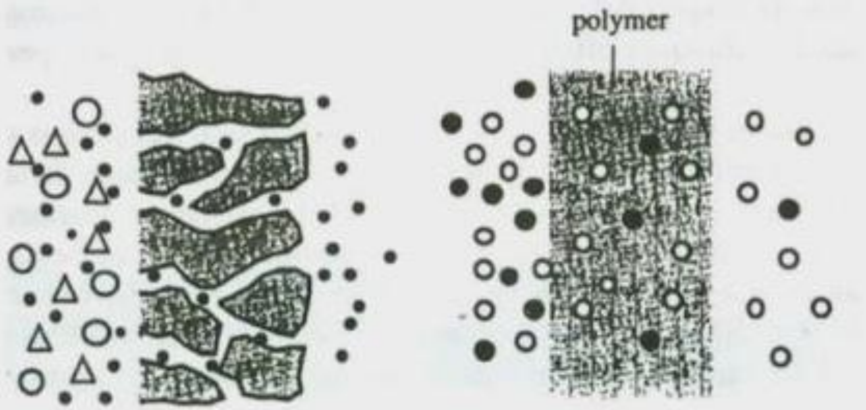


Fig. Schematic drawing of a porous and nonporous membrane

Porous and Non-porous Membranes

- In microfiltration/ultrafiltration membranes, fixed pores are present which can be characterized by several techniques.
- In order to avoid confusion in defining porous membranes the term **'porous'** has been used through out this course for both the microfiltration and ultrafiltration membranes instead of the frequently used definition of microporous.
- The definition of porous is more in agreement with the definitions adopted by the IUPAC.

  - macropores > 50 nm

  - mesopores 2 nm < pore size < 50 nm

  - micropores < 2 nm.

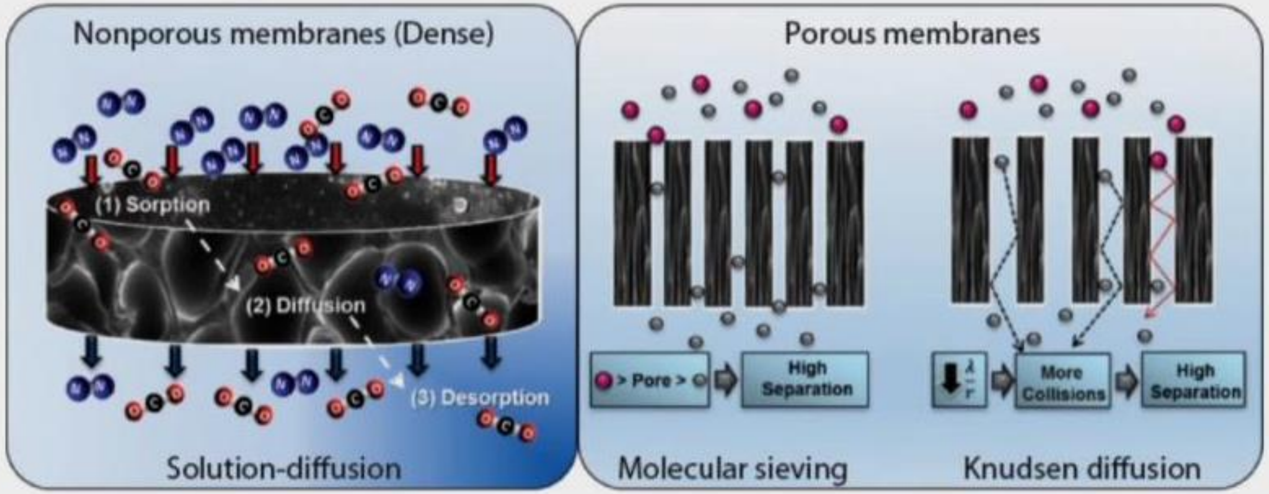


Fig. Membrane gas permeation mechanism through porous and non-porous membranes

- The separation characteristics are determined by the large pores in the membrane.
- ***Surface porosity*** is also a very important variable in determining the flux through the membrane, in combination with the ***thickness of the top layer*** or the ***length of the pore***.
- Different microfiltration membranes exhibit a wide range of surface porosity and the ultrafiltration membranes normally show very low surface porosities, ranging from 0.1-1%.

Two different types of characterization methods for porous membrane can be distinguished from the discussed considerations:

Structure related parameters:

- Determination of pore size, pore size distribution, top layer thickness and surface porosity.

Permeation related parameters:

- Determination of the actual separation parameters using solutes that are more or less retained by the membrane (*'cut-off'* measurement)
- It is often very difficult to relate the structure-related parameters directly to the permeation related parameters because the pore size and shape is not very well defined.

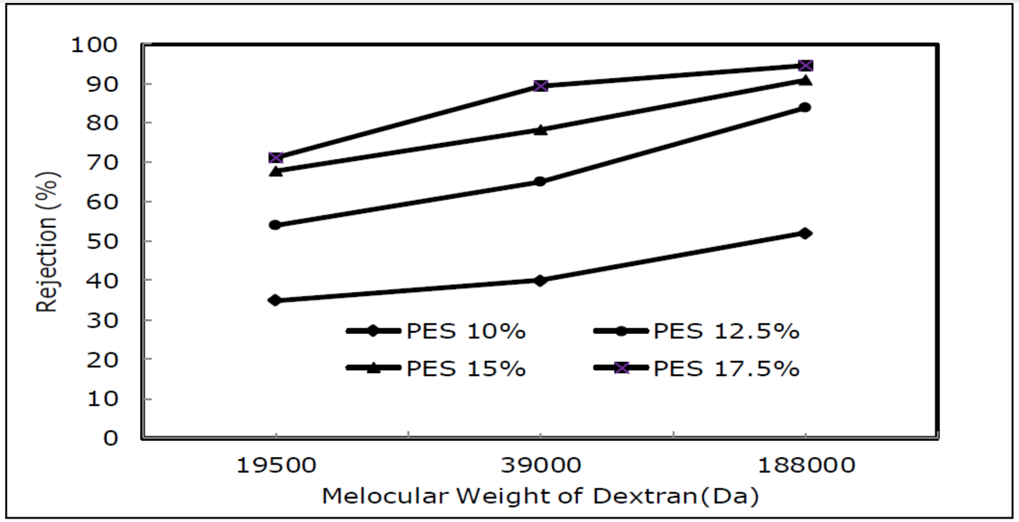


Figure 2. Rejection of Membrane as Function of Molecular Weight of Dextran

The characterization of porous membranes

- The configuration of the pores (cylindrical, packed-spheres) used in simple model descriptions deviate sometimes dramatically from the actual morphology, as depicted schematically below.
- A combination of well defined characterization techniques can give information about membrane morphology which can be used as a first estimate in determining possible fields of application.

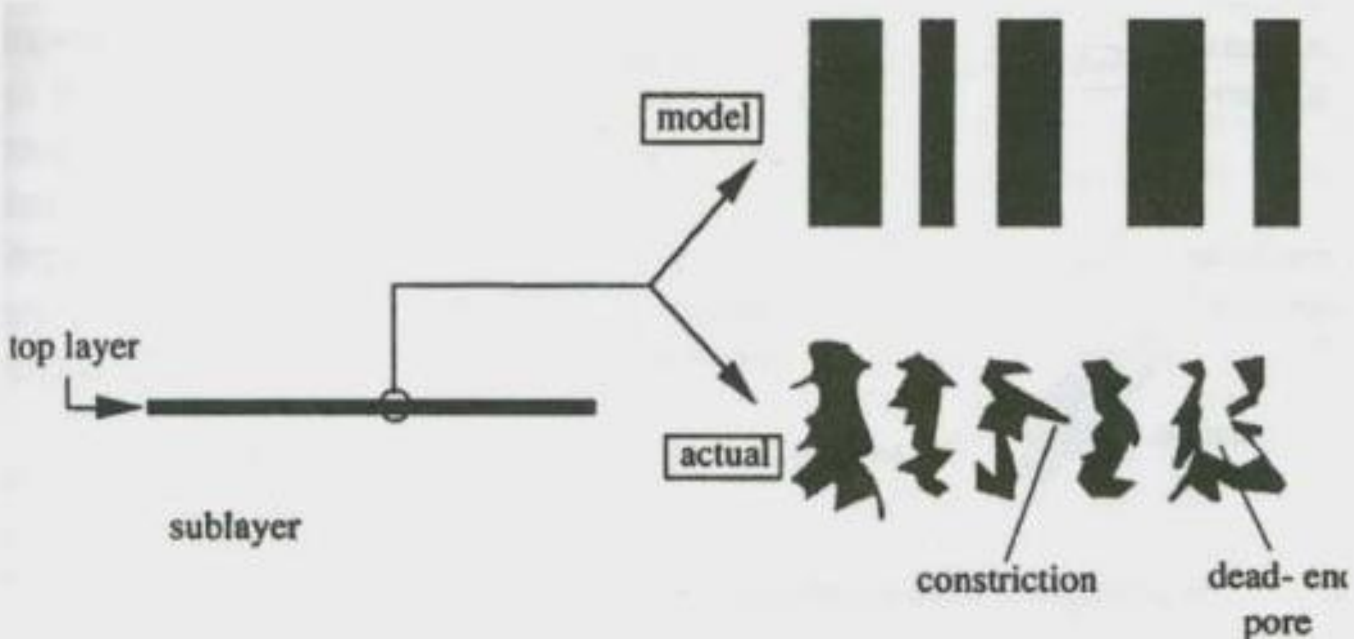
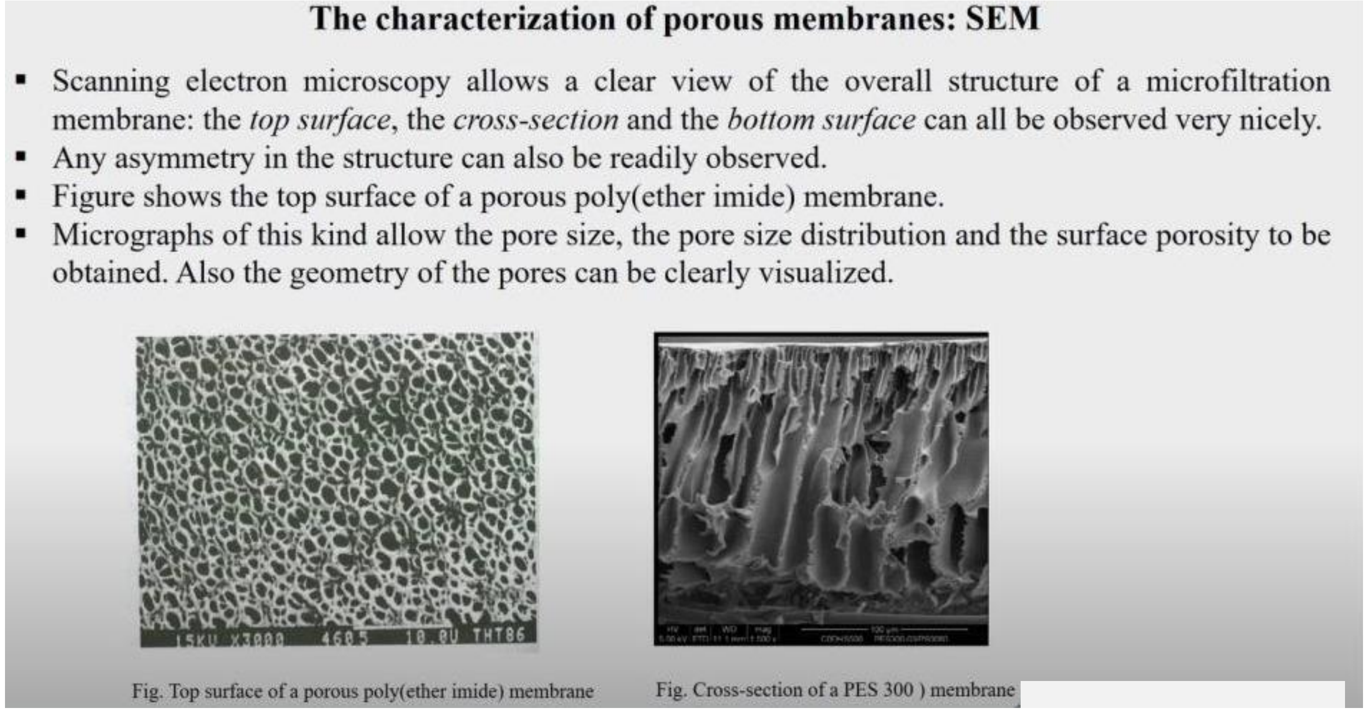


Fig. Comparison of an ideal and the actual structure in the top layer of an ultrafiltration membrane

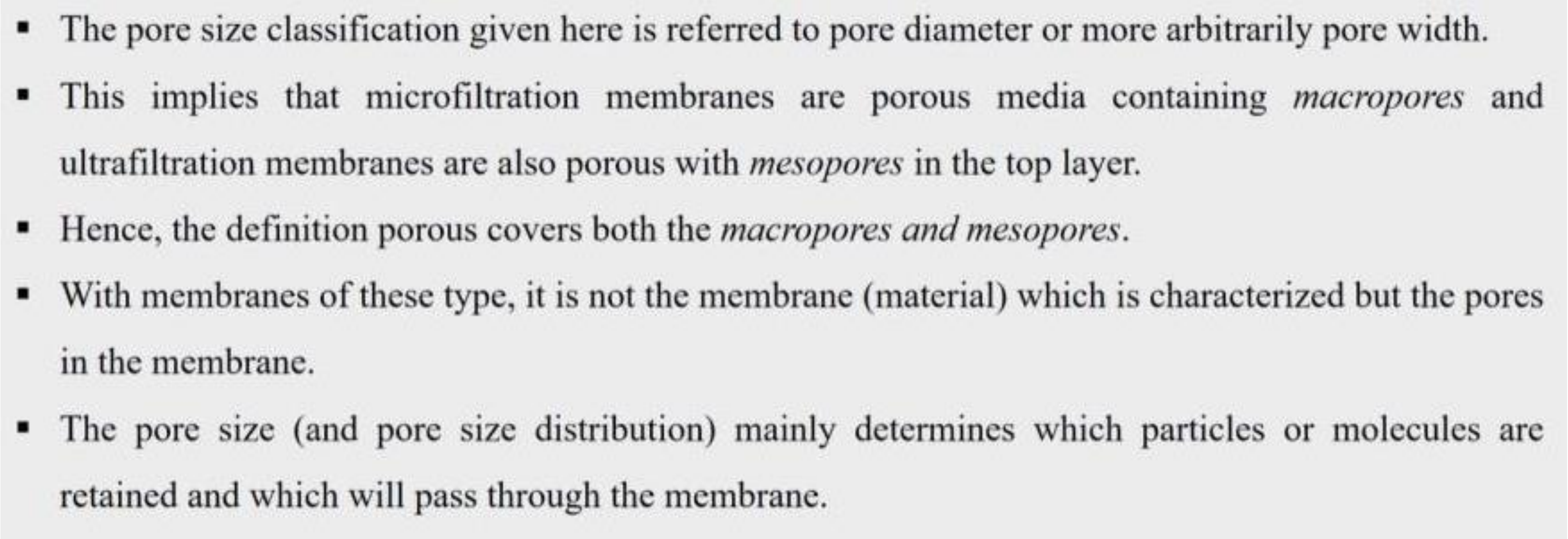


The characterization of porous membranes: SEM

- Scanning electron microscopy allows a clear view of the overall structure of a microfiltration membrane: the *top surface*, the *cross-section* and the *bottom surface* can all be observed very nicely.
- Any asymmetry in the structure can also be readily observed.
- Figure shows the top surface of a porous poly(ether imide) membrane.
- Micrographs of this kind allow the pore size, the pore size distribution and the surface porosity to be obtained. Also the geometry of the pores can be clearly visualized.

Fig. Top surface of a porous poly(ether imide) membrane

Fig. Cross-section of a PES 300) membrane



- The pore size classification given here is referred to pore diameter or more arbitrarily pore width.
- This implies that microfiltration membranes are porous media containing *macropores* and ultrafiltration membranes are also porous with *mesopores* in the top layer.
- Hence, the definition porous covers both the *macropores and mesopores*.
- With membranes of these type, it is not the membrane (material) which is characterized but the pores in the membrane.
- The pore size (and pore size distribution) mainly determines which particles or molecules are retained and which will pass through the membrane.

Membranes Transport Theory

- The most important property of membranes is their ability to control the rate of permeation of different species.
- Permeation mechanism can be explained by
  - Transport through porous membrane (MF and UF)

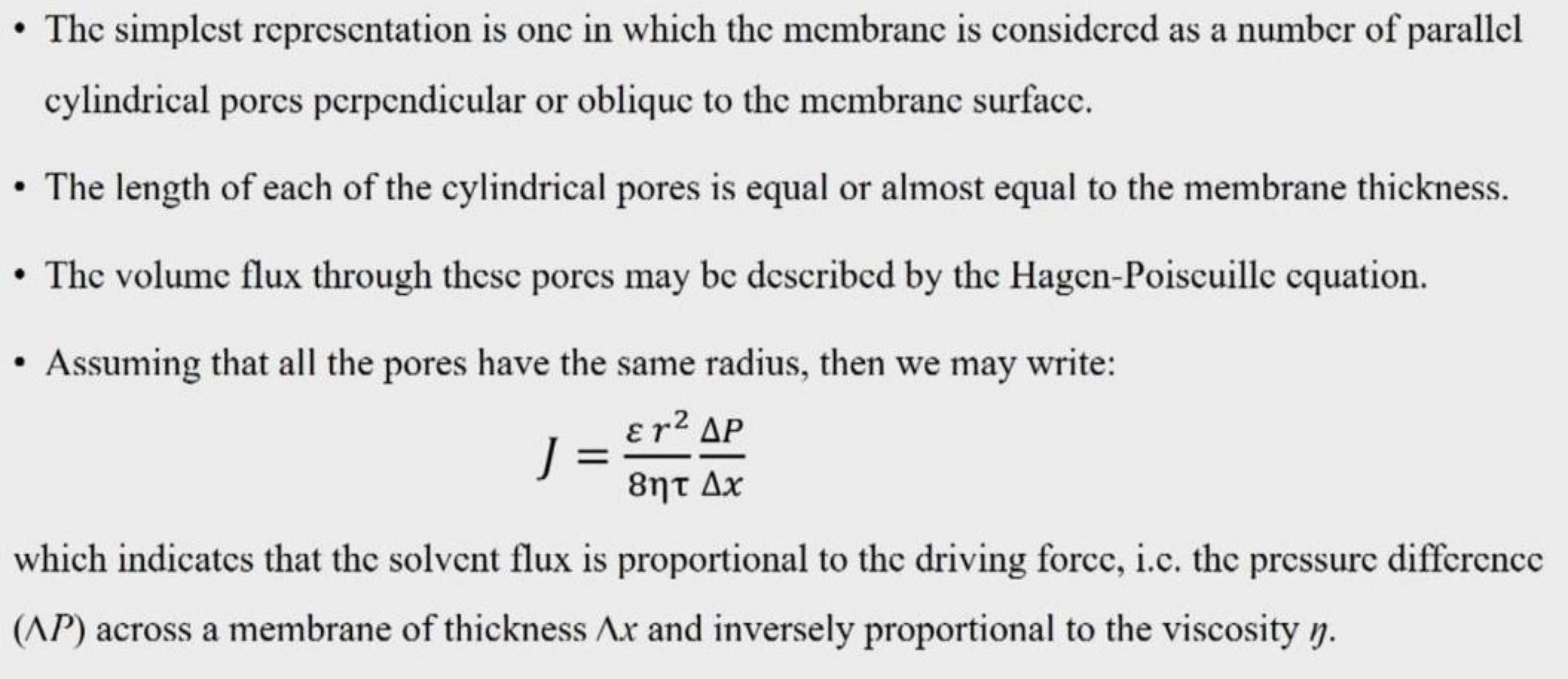
    Separation occurs through pores
  - Transport through non-porous membrane (Dense membranes)

    Permeants dissolve in the membrane material and then diffuse through the membrane down a concentration gradient.

Transport through porous membranes

- Porous membranes are used in microfiltration and ultrafiltration processes.
- Here the *resistance* is determined by the *total membrane thickness*.

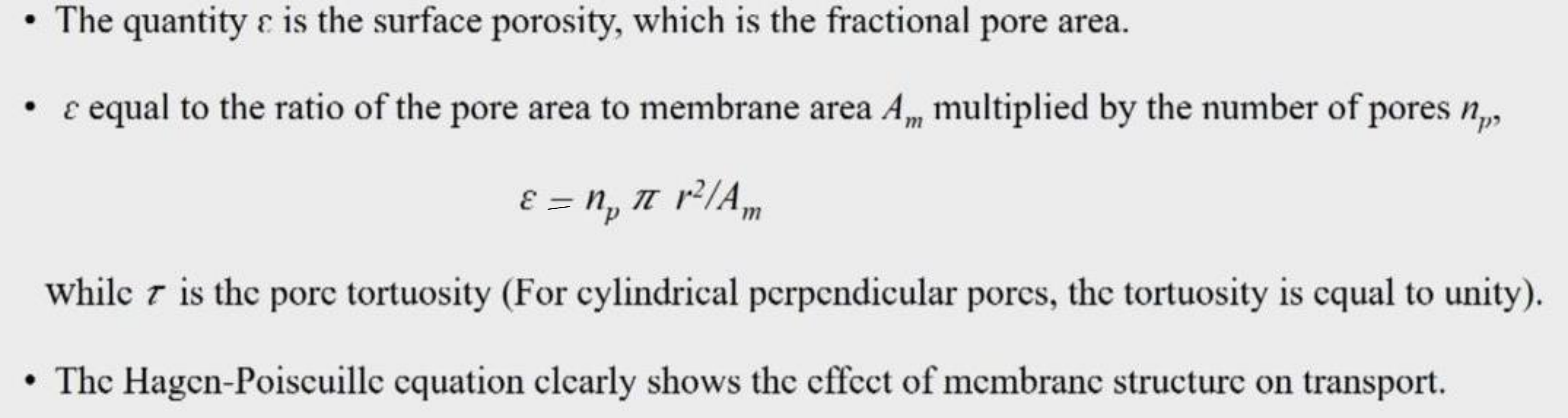
Figure. Some characteristic pore geometries found in porous membranes



- The simplest representation is one in which the membrane is considered as a number of parallel cylindrical pores perpendicular or oblique to the membrane surface.
- The length of each of the cylindrical pores is equal or almost equal to the membrane thickness.
- The volume flux through these pores may be described by the Hagen-Poiseuille equation.
- Assuming that all the pores have the same radius, then we may write:

$$J = \frac{\varepsilon\, r^2}{8\eta\tau} \frac{\Delta P}{\Delta x}$$

which indicates that the solvent flux is proportional to the driving force, i.e. the pressure difference (ΛP) across a membrane of thickness Λx and inversely proportional to the viscosity η.

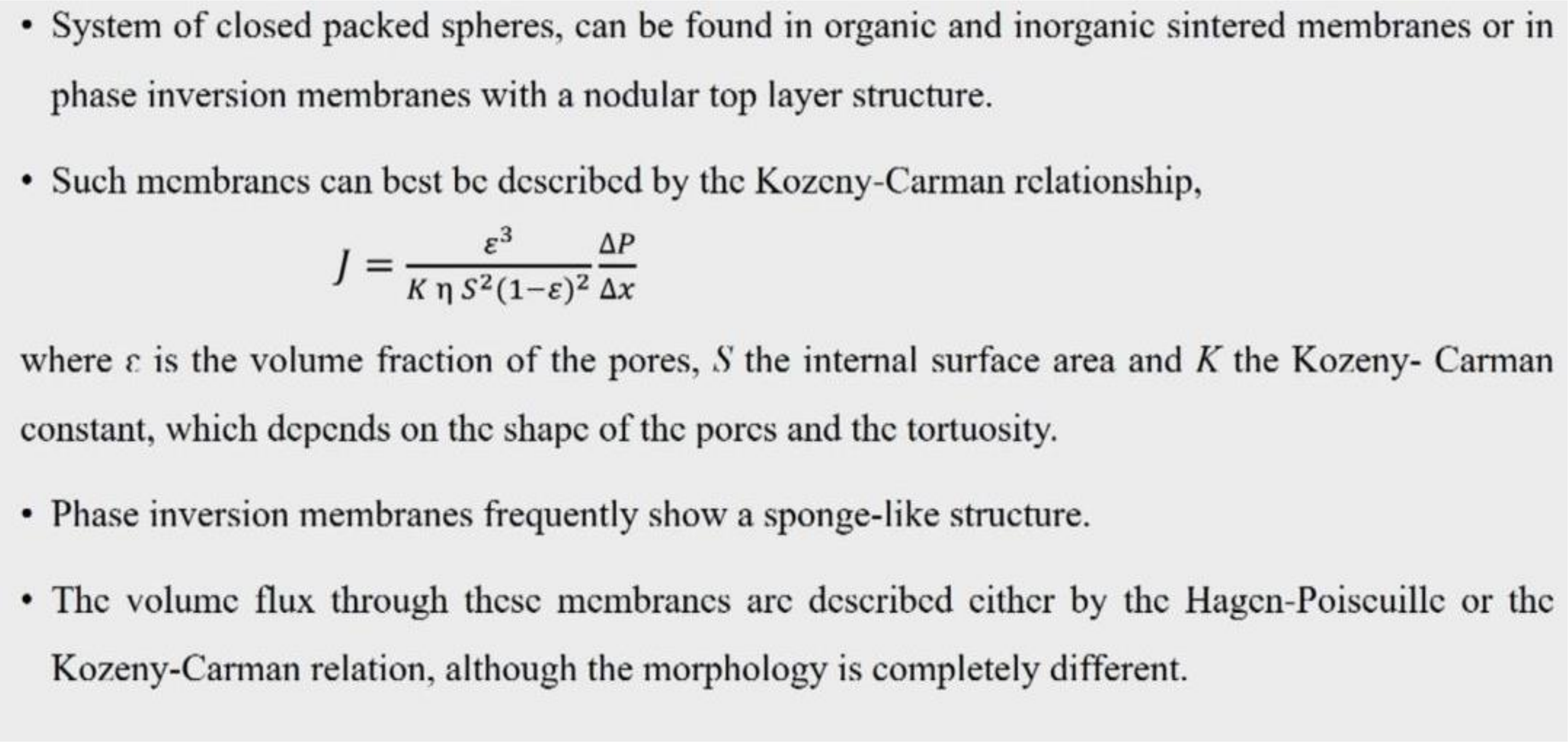


- The quantity ε is the surface porosity, which is the fractional pore area.
- ε equal to the ratio of the pore area to membrane area A_m multiplied by the number of pores n_p,

$$\varepsilon = n_p\, \pi\, r^2 / A_m$$

while τ is the pore tortuosity (For cylindrical perpendicular pores, the tortuosity is equal to unity).

- The Hagen-Poiseuille equation clearly shows the effect of membrane structure on transport.



- System of closed packed spheres, can be found in organic and inorganic sintered membranes or in phase inversion membranes with a nodular top layer structure.
- Such membranes can best be described by the Kozeny-Carman relationship,

$$J = \frac{\varepsilon^3}{K\,\eta\,S^2(1-\varepsilon)^2}\frac{\Delta P}{\Delta x}$$

where ε is the volume fraction of the pores, S the internal surface area and K the Kozeny- Carman constant, which depends on the shape of the pores and the tortuosity.

- Phase inversion membranes frequently show a sponge-like structure.
- The volume flux through these membranes are described either by the Hagen-Poiseuille or the Kozeny-Carman relation, although the morphology is completely different.

Transport of gases through porous membranes

- When an asymmetric membrane or composite membrane is used in gas separation, the gas molecules will tend to diffuse from the high-pressure to the low-pressure side.
- Various transport mechanisms can be distinguished depending on the structure of the asymmetric membrane or composite membrane,

a) Transport through a dense (nonporous) layer

b) Knudsen flow in narrow pores

c) Viscous flow in wide pores

d) Surface diffusion along the pore wall

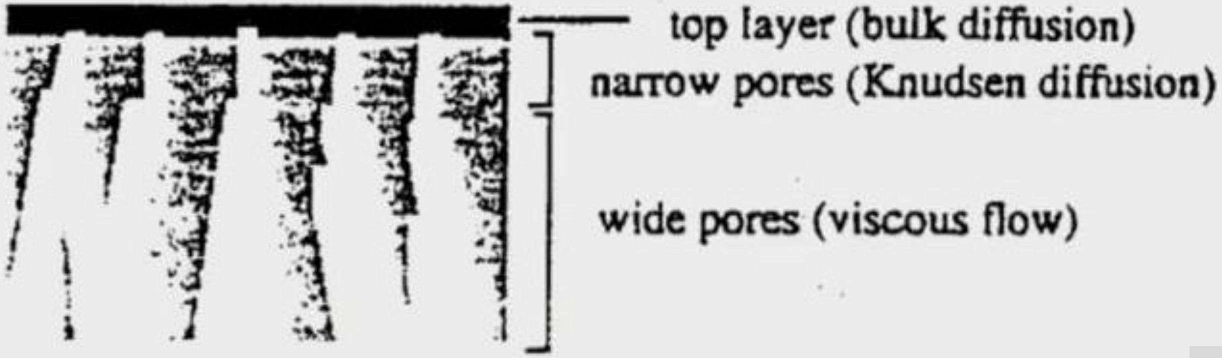


Fig: Transport in an asymmetric membrane as a result of various mechanisms

- The rate determining step is mostly transport through the dense nonporous top layer.
- However, it is also possible that the other mechanisms contribute to transport, i.e. the resistance of the sublayer may contribute to transport.
- In addition, generally ultrafiltration types of membranes are employed as sublayer.
- This implies that the effective thickness is much larger than the actual top layer thickness, as depicted in below figure.

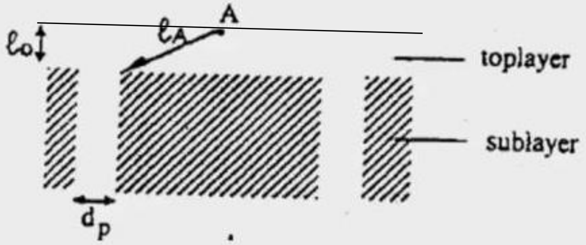
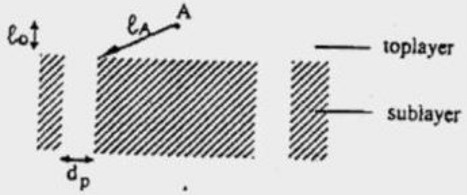


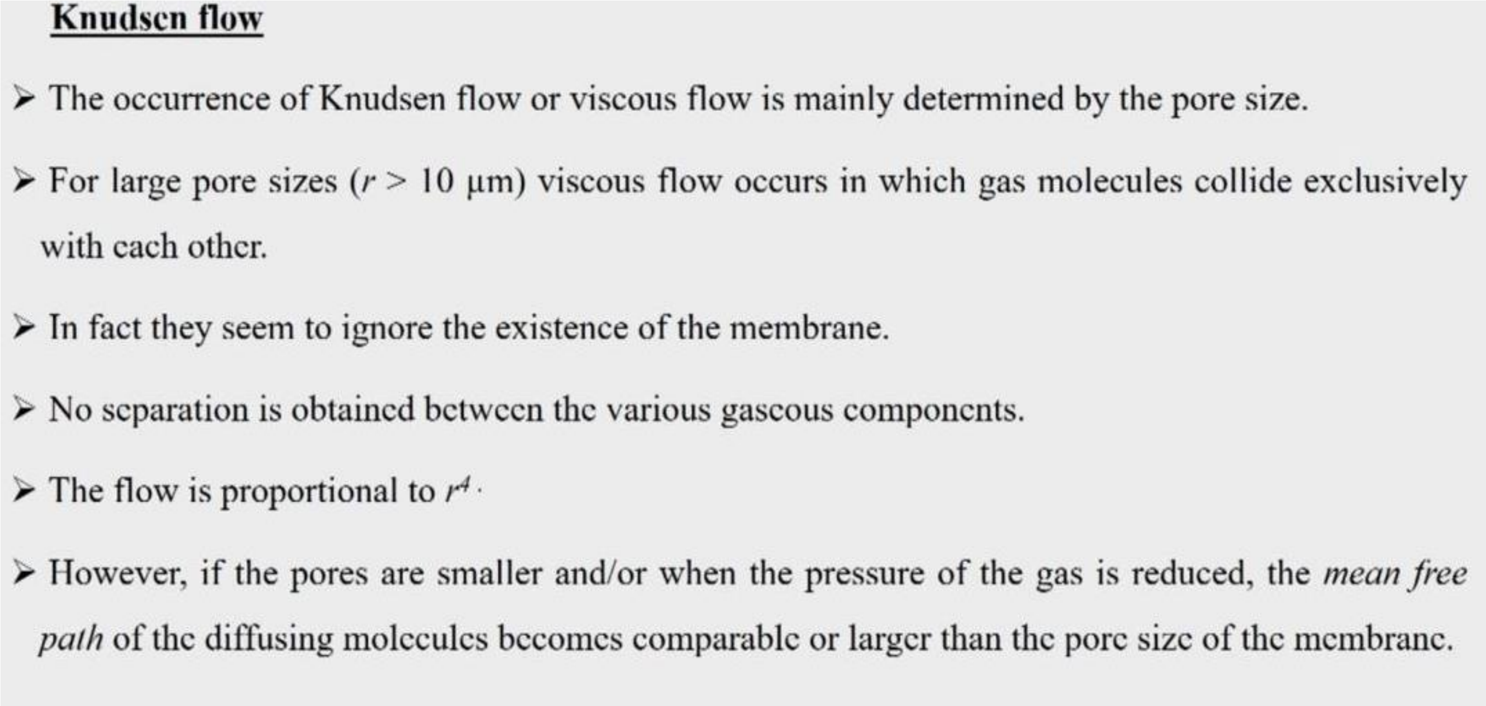
Fig: Schematic drawing of various diffusion paths in a composite membrane

- The actual top layer thickness is l_o but when a molecule penetrates the film at point A the thickness is much larger as shown in the figure.
- It is obvious that the effective thickness l_{eff} is strongly dependent on the surface porosity ε of the sublayer.
- The average diffusion length can be given by,

$$l_{eff} = \varepsilon\, l_o + (1 - \epsilon)\frac{l_A\, l_o}{2}$$

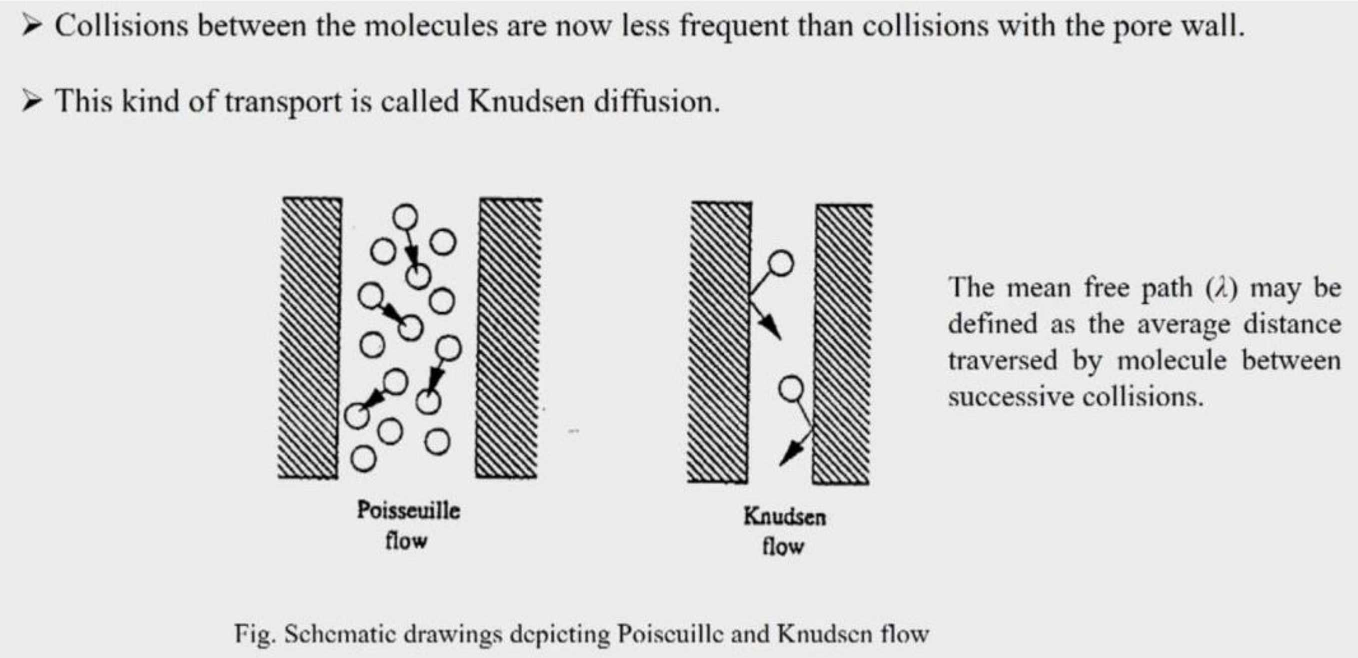


- This equation shows clearly that the determination of the P/l value, which is often used to characterize the resistance of the sublayer, is not sufficient and that data are required to determine the pore size distribution.



Knudsen flow

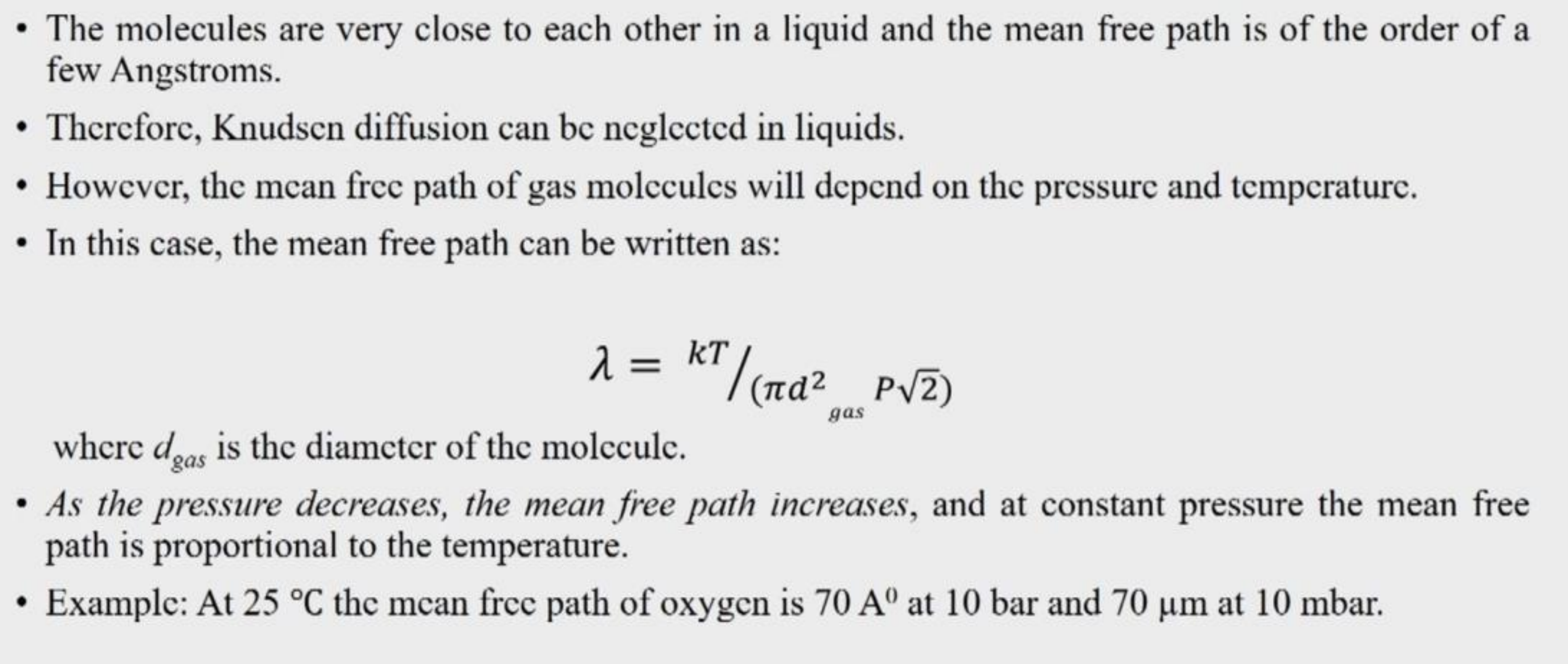
- The occurrence of Knudsen flow or viscous flow is mainly determined by the pore size.
- For large pore sizes ($r > 10\ \mu m$) viscous flow occurs in which gas molecules collide exclusively with each other.
- In fact they seem to ignore the existence of the membrane.
- No separation is obtained between the various gaseous components.
- The flow is proportional to r^4.
- However, if the pores are smaller and/or when the pressure of the gas is reduced, the *mean free path* of the diffusing molecules becomes comparable or larger than the pore size of the membrane.



- Collisions between the molecules are now less frequent than collisions with the pore wall.
- This kind of transport is called Knudsen diffusion.

The mean free path (λ) may be defined as the average distance traversed by molecule between successive collisions.

Fig. Schematic drawings depicting Poiseuille and Knudsen flow

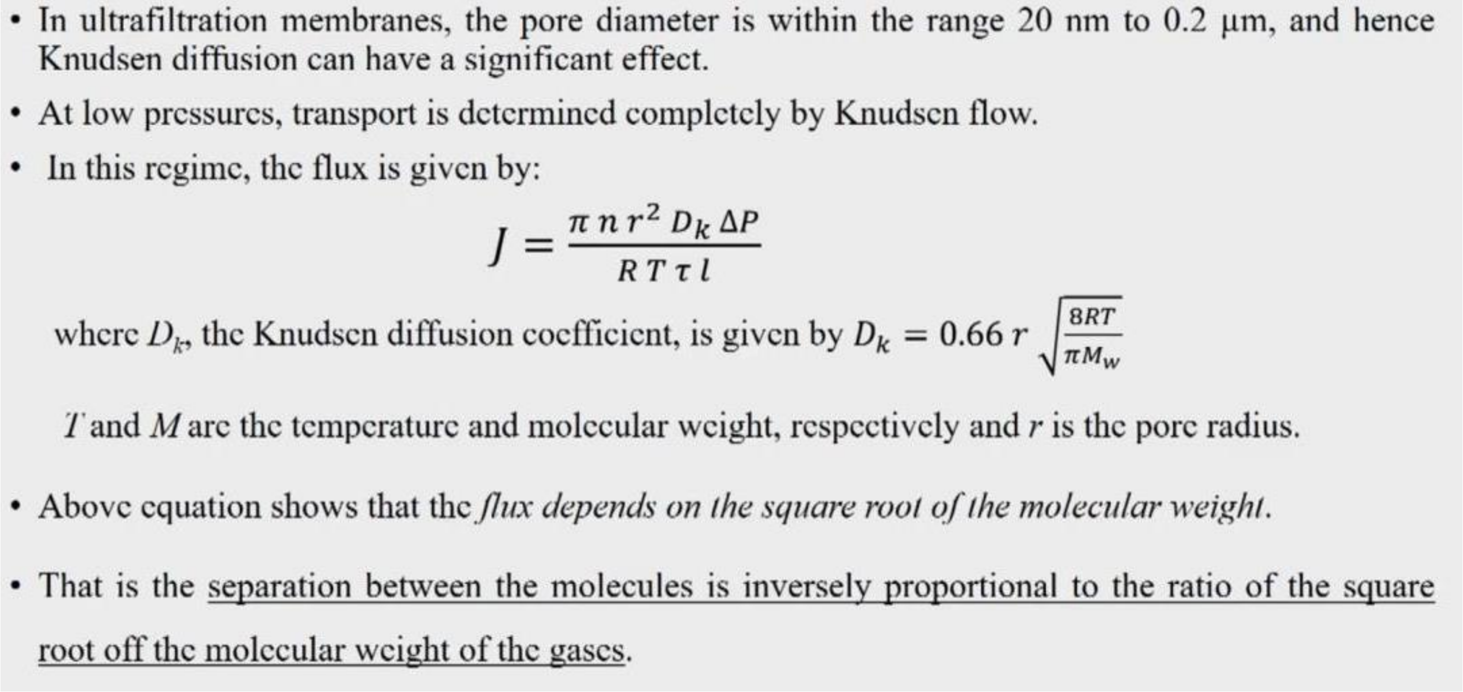


- The molecules are very close to each other in a liquid and the mean free path is of the order of a few Angstroms.
- Therefore, Knudsen diffusion can be neglected in liquids.
- However, the mean free path of gas molecules will depend on the pressure and temperature.
- In this case, the mean free path can be written as:

$$\lambda = {}^{kT}\!\big/\!\left(\pi d^2_{gas}\, P\sqrt{2}\right)$$

where d_{gas} is the diameter of the molecule.

- *As the pressure decreases, the mean free path increases*, and at constant pressure the mean free path is proportional to the temperature.
- Example: At 25 °C the mean free path of oxygen is $70\ A^0$ at 10 bar and 70 µm at 10 mbar.



- In ultrafiltration membranes, the pore diameter is within the range 20 nm to 0.2 µm, and hence Knudsen diffusion can have a significant effect.
- At low pressures, transport is determined completely by Knudsen flow.
- In this regime, the flux is given by:

$$J = \frac{\pi\, n\, r^2\, D_k\, \Delta P}{R\, T\, \tau\, l}$$

where D_k, the Knudsen diffusion coefficient, is given by $D_k = 0.66\, r\sqrt{\frac{8RT}{\pi M_w}}$

T and *M* are the temperature and molecular weight, respectively and *r* is the pore radius.

- Above equation shows that the *flux depends on the square root of the molecular weight*.
- That is the separation between the molecules is inversely proportional to the ratio of the square root off the molecular weight of the gases.

Friction model

- Another approach used to describe transport through a porous membrane is the friction model.
- This considers that passage through the porous membrane occurs both by *viscous flow and diffusion.*
- This implies that the pore sizes are so small that the solute molecules cannot pass freely through the pore, and that *friction occurs between the solute and the pore wall* and also *between the solvent and the pore wall* and *between the solvent and the solute.*
- The frictional force F per mole is related linearly to the velocity difference or relative velocity.
- The proportionality factor is called the friction coefficient, f.
- On considering permeation of the solvent and solute through a membrane and taking the membrane as a frame of reference ($V_m = 0$), the following frictional forces can be distinguished,

  (subscripts s, w and m refer to solute, water (solvent) and membrane respectively):

$$F_{sm} = -f_{sm}.(V_s - V_m) = -f_{sm}.V_s$$

$$F_{wm} = -f_{wm}.(V_w - V_m) = -f_{wm}.V_w$$

$$F_{sw} = -f_{sw}.(V_s - V_w)$$

$$F_{ws} = -f_{ws}.(V_w - V_s)$$

- The proportionality factor f_{sm} (the friction coefficient) denotes interaction *between the solute and the polymer (pore wall).*
- Using linear relationships between the fluxes and forces in accordance with the concept of irreversible thermodynamics and assuming isothermal conditions the forces can be described as the gradient of the chemical potential, i.e.

$$X_i = -\frac{\partial \mu_i}{\partial x}$$

- ➢ However, other (external) forces acting on component *i*, such as the frictional force, must also be included. Thus, earlier equation becomes,

$$X_i = -\frac{\partial \mu_i}{\partial x} + F_i$$

- ➢ The *diffusive solute flux* can be written as the product of the mobility, concentration and driving force.
- ➢ The mobility *m* may be defined as,

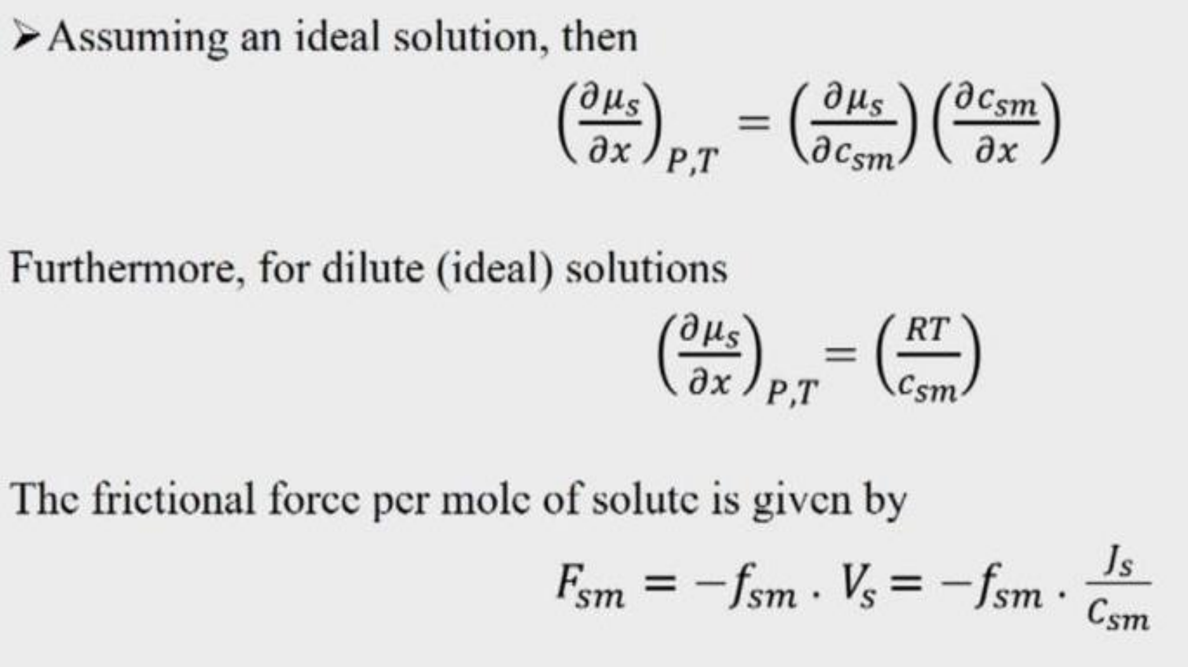
$$m = {}^{D}/_{RT}$$

so that the solute flux then becomes,

$$J_s = m_{ws}\, c_{sm}\left(-\frac{\partial \mu_s}{\partial x} + F_{sm}\right)$$

where c_{sm} is the concentration of the solute in the membrane (pore).

- ➢ The above describes the solute flux as a combination of diffusion (first term on the right-hand side) and viscous flow (second term on the right-hand side).



- Assuming an ideal solution, then

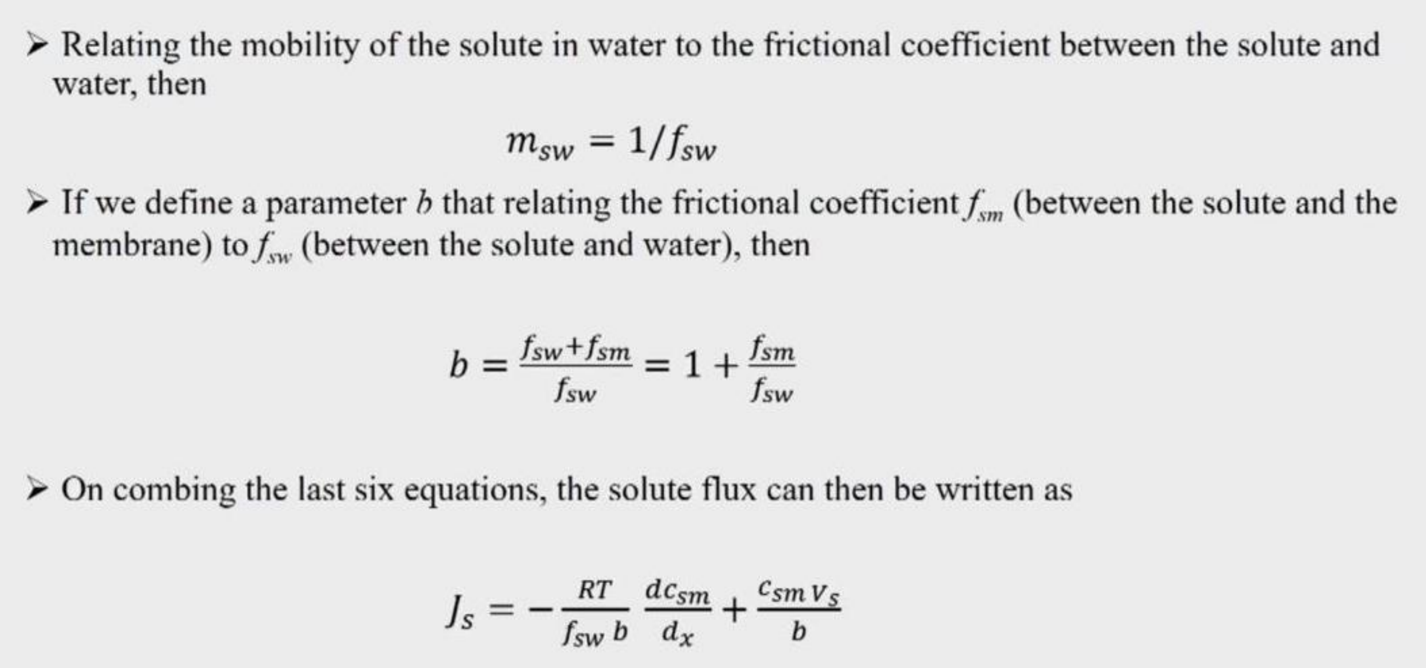
$$\left(\frac{\partial \mu_s}{\partial x}\right)_{P,T} = \left(\frac{\partial \mu_s}{\partial c_{sm}}\right)\left(\frac{\partial c_{sm}}{\partial x}\right)$$

Furthermore, for dilute (ideal) solutions

$$\left(\frac{\partial \mu_s}{\partial x}\right)_{P,T} = \left(\frac{RT}{c_{sm}}\right)$$

The frictional force per mole of solute is given by

$$F_{sm} = -f_{sm} \cdot V_s = -f_{sm} \cdot \frac{J_s}{C_{sm}}$$



- Relating the mobility of the solute in water to the frictional coefficient between the solute and water, then

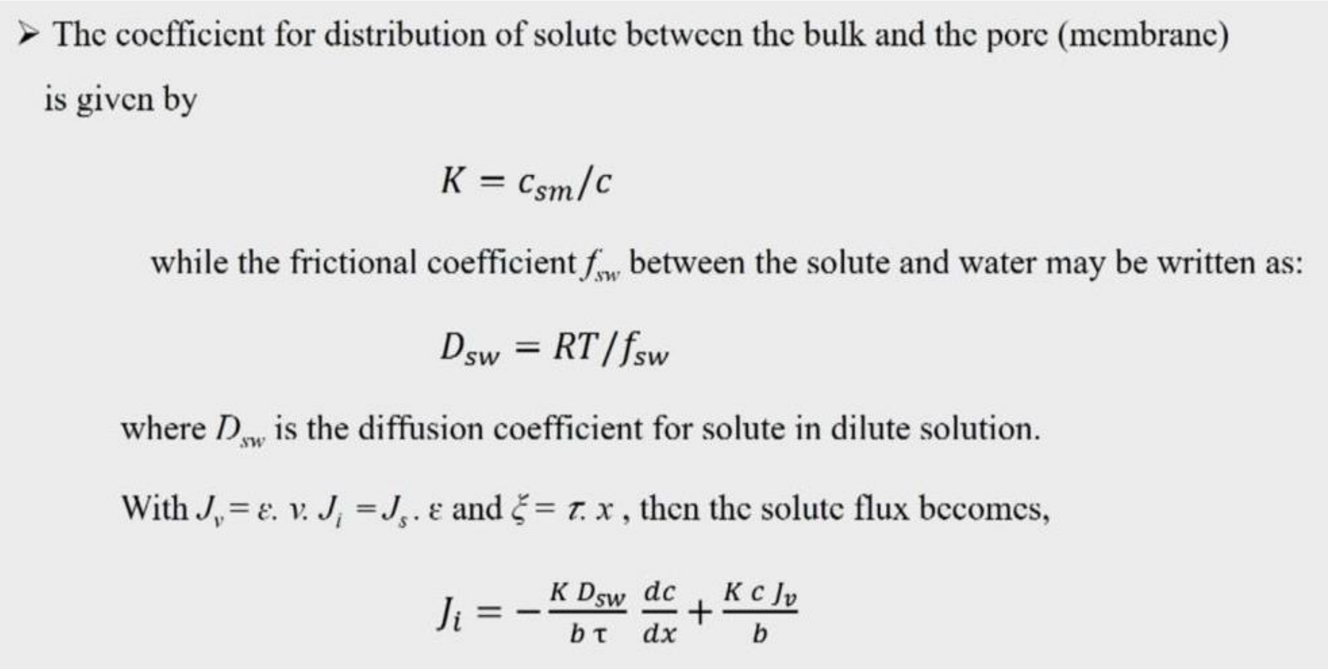
$$m_{sw} = 1/f_{sw}$$

- If we define a parameter b that relating the frictional coefficient f_{sm} (between the solute and the membrane) to f_{sw} (between the solute and water), then

$$b = \frac{f_{sw}+f_{sm}}{f_{sw}} = 1 + \frac{f_{sm}}{f_{sw}}$$

- On combing the last six equations, the solute flux can then be written as

$$J_s = -\frac{RT}{f_{sw}\, b}\,\frac{dc_{sm}}{d_x} + \frac{c_{sm}\, V_s}{b}$$



- The coefficient for distribution of solute between the bulk and the pore (membrane) is given by

$$K = c_{sm}/c$$

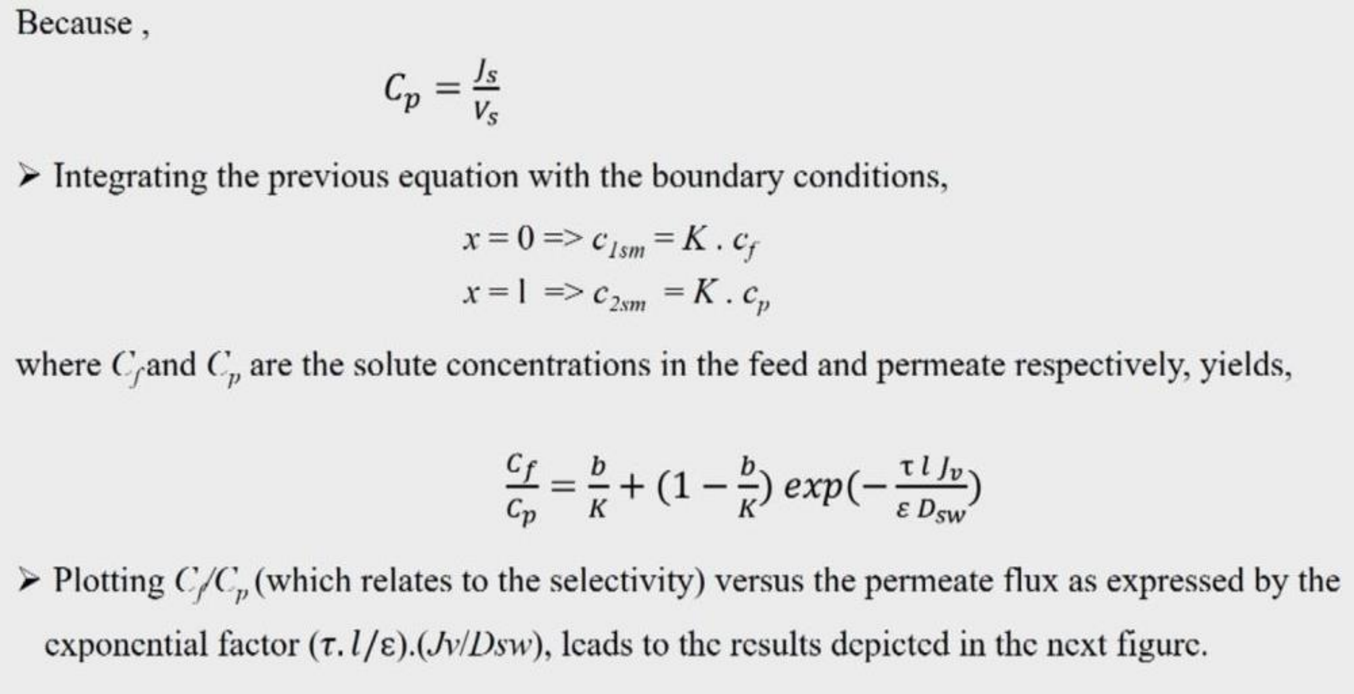
while the frictional coefficient f_{sw} between the solute and water may be written as:

$$D_{sw} = RT/f_{sw}$$

where D_{sw} is the diffusion coefficient for solute in dilute solution.

With $J_v = \varepsilon .\ v.\ J_i = J_s .\ \varepsilon$ and $\xi = \tau .\ x$, then the solute flux becomes,

$$J_i = -\frac{K\, D_{sw}}{b\, \tau}\,\frac{dc}{dx} + \frac{K\, c\, J_v}{b}$$



Because ,

$$C_p = \frac{J_s}{V_s}$$

- Integrating the previous equation with the boundary conditions,

$$x = 0 \Rightarrow c_{1sm} = K \,.\, c_f$$
$$x = l \Rightarrow c_{2sm} = K \,.\, c_p$$

where C_f and C_p are the solute concentrations in the feed and permeate respectively, yields,

$$\frac{C_f}{C_p} = \frac{b}{K} + \left(1 - \frac{b}{K}\right) exp\left(-\frac{\tau\, l\, J_v}{\varepsilon\, D_{sw}}\right)$$

- Plotting C_f/C_p (which relates to the selectivity) versus the permeate flux as expressed by the exponential factor $(\tau . l/\varepsilon).(Jv/Dsw)$, leads to the results depicted in the next figure.

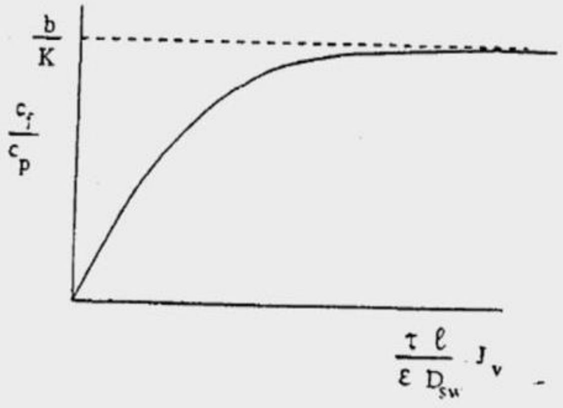


Figure. Schematic drawing of concentration reduction (c_f/c_p) versus flux.

- This figure demonstrates that the ratio c_f/c_p increases to attain an asymptotic value at b/K, a factor which has a maximum value when b is large and K is small.

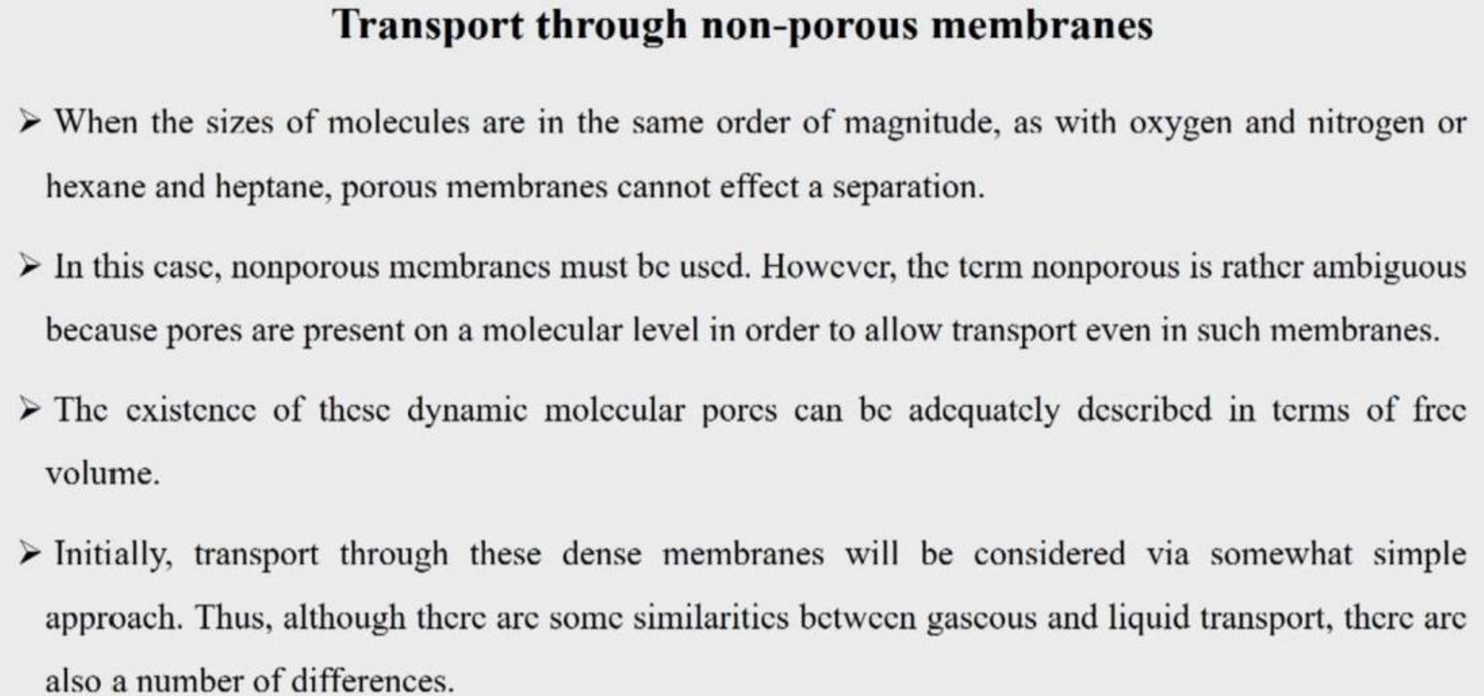
- The friction factor b is large when the friction between the solute and the membrane (f_{sm}) is greater than the fiction between the solute and the solvent (f_{sw}).
- The parameter K is small when the uptake of solute by the membrane from the feed is small compared to the solvent (water) uptake, i.e. when the solute distribution coefficient is small.
- An important point is that both the distribution coefficient (an equilibrium thermodynamic parameter) and the frictional forces (kinetic parameter) determine the selectivity.

Solute rejection is given by

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

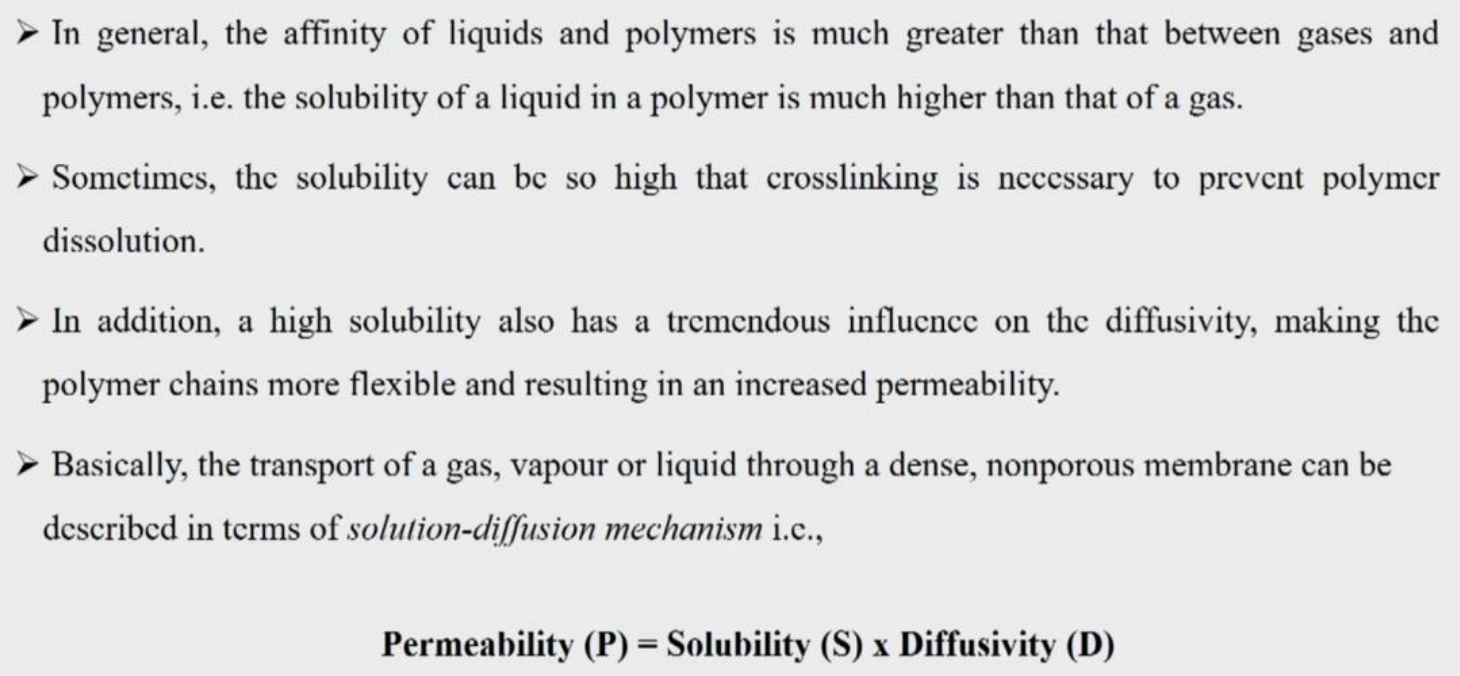
- From earlier equation of C_f/C_p we can seen that the maximum rejection R_{max} ($Jv = \infty$) is given by,

$$R_{max} = \sigma = 1 - \frac{K}{b} = 1 - \frac{K}{\left[1 + \frac{fsm}{fsw}\right]^{-1}}$$



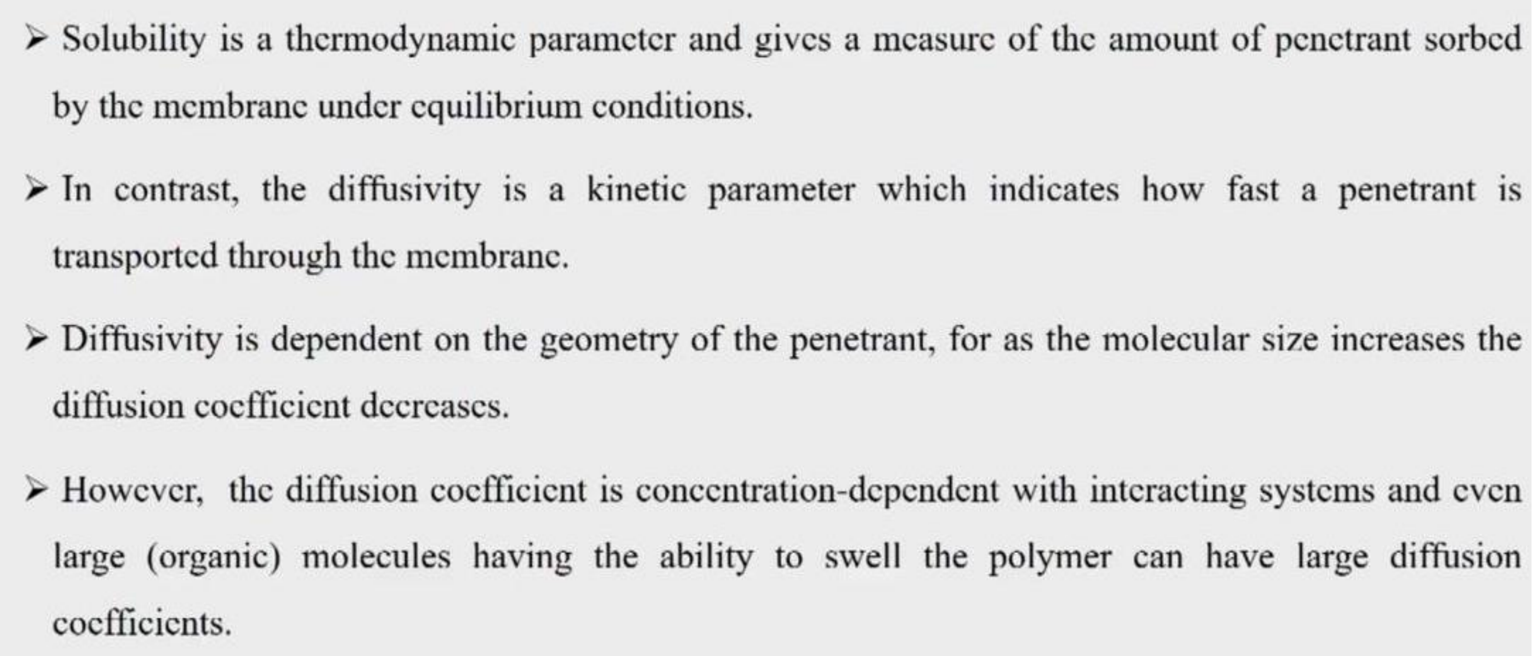
Transport through non-porous membranes

- When the sizes of molecules are in the same order of magnitude, as with oxygen and nitrogen or hexane and heptane, porous membranes cannot effect a separation.
- In this case, nonporous membranes must be used. However, the term nonporous is rather ambiguous because pores are present on a molecular level in order to allow transport even in such membranes.
- The existence of these dynamic molecular pores can be adequately described in terms of free volume.
- Initially, transport through these dense membranes will be considered via somewhat simple approach. Thus, although there are some similarities between gaseous and liquid transport, there are also a number of differences.

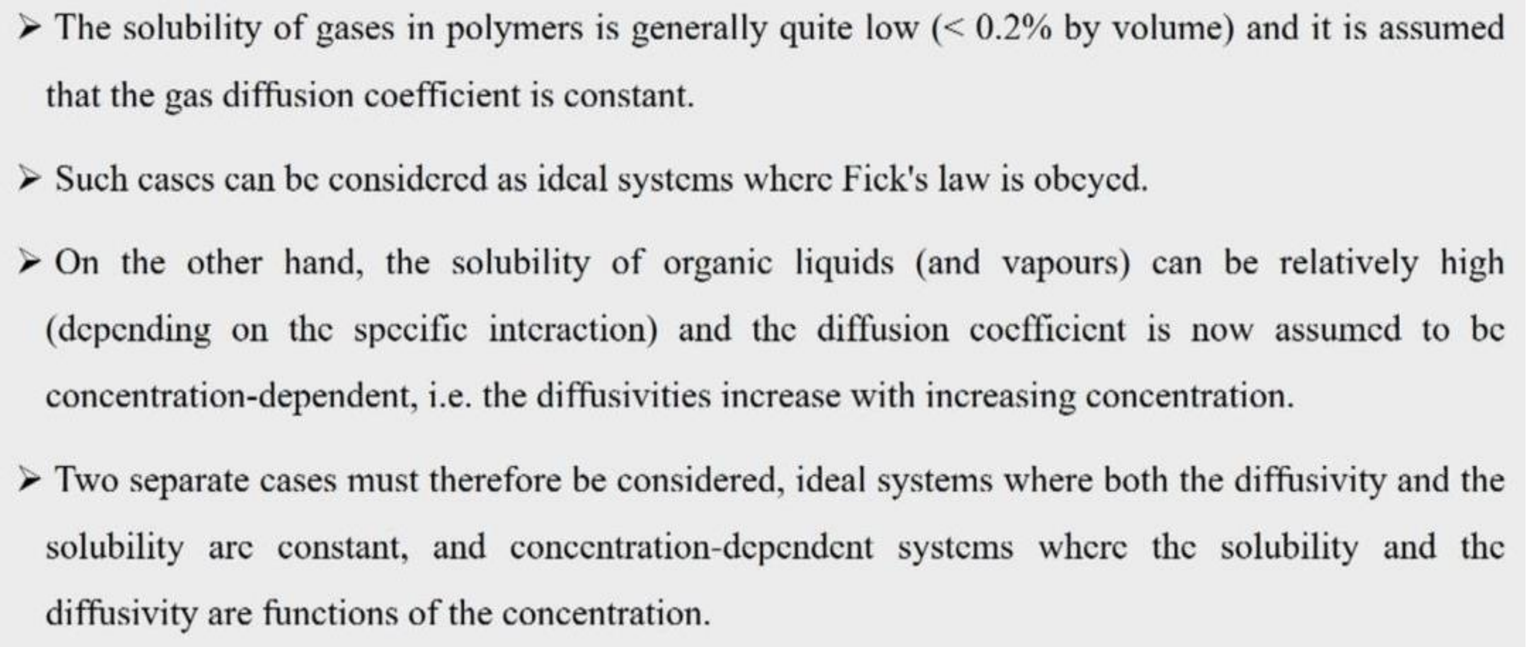


- In general, the affinity of liquids and polymers is much greater than that between gases and polymers, i.e. the solubility of a liquid in a polymer is much higher than that of a gas.
- Sometimes, the solubility can be so high that crosslinking is necessary to prevent polymer dissolution.
- In addition, a high solubility also has a tremendous influence on the diffusivity, making the polymer chains more flexible and resulting in an increased permeability.
- Basically, the transport of a gas, vapour or liquid through a dense, nonporous membrane can be described in terms of *solution-diffusion mechanism* i.e.,

Permeability (P) = Solubility (S) x Diffusivity (D)



- Solubility is a thermodynamic parameter and gives a measure of the amount of penetrant sorbed by the membrane under equilibrium conditions.
- In contrast, the diffusivity is a kinetic parameter which indicates how fast a penetrant is transported through the membrane.
- Diffusivity is dependent on the geometry of the penetrant, for as the molecular size increases the diffusion coefficient decreases.
- However, the diffusion coefficient is concentration-dependent with interacting systems and even large (organic) molecules having the ability to swell the polymer can have large diffusion coefficients.



- The solubility of gases in polymers is generally quite low (< 0.2% by volume) and it is assumed that the gas diffusion coefficient is constant.
- Such cases can be considered as ideal systems where Fick's law is obeyed.
- On the other hand, the solubility of organic liquids (and vapours) can be relatively high (depending on the specific interaction) and the diffusion coefficient is now assumed to be concentration-dependent, i.e. the diffusivities increase with increasing concentration.
- Two separate cases must therefore be considered, ideal systems where both the diffusivity and the solubility are constant, and concentration-dependent systems where the solubility and the diffusivity are functions of the concentration.

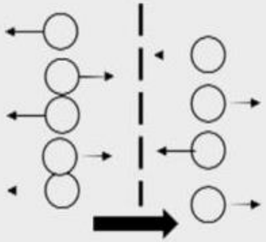


Fig. Diffusion as a result of random molecular motions.

- Permeability is both a function of solubility and diffusivity.
- The simplest way to describe the transport of gases through membranes is via Fick's first law.

$$J = -D\frac{dc}{dx}$$

- The flux *J* of a component through a plane perpendicular to the direction of diffusion being proportional to the concentration gradient *dc*/*dx*.
- The proportionality constant is called the *diffusion coefficient*.
- Diffusion may be considered as statistical molecular transport as a result of the random motion of the molecules.

Determination of the diffusion coefficient

- The diffusion coefficient is constant for ideal systems as discussed here and can be determined by a permeation method (the time-lag method).
- If the membrane is free of penetrant at the start of the experiment the amount of penetrant (*Q*) passing through the membrane in the time *t*,

$$\frac{Q_t}{lc_i} = \frac{Dt}{l^2} - \frac{1}{6} - \frac{2}{\pi}\sum \frac{(-1)^n}{n^2} exp\left[\frac{-D\, n^2\pi^2\, t}{l^2}\right]$$

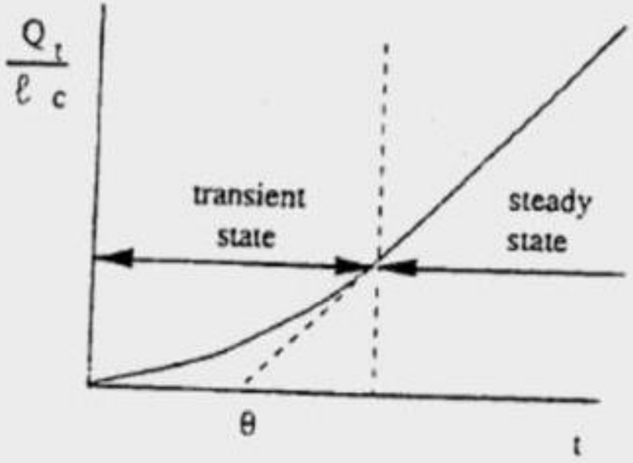
where *c*, is the concentration on the feed side and *n* is an integer.

- A curved plot can be observed initially in the transient state but this becomes linear with time as steady-state conditions are attained. When $t \to \infty$, the exponential term in above Eq. can be neglected and it simplifies to:

$$Q_t = \frac{DC_i}{l}\left(t - \frac{l^2}{6D}\right)$$

- If the linear plot of $Q_t / (l.c_i)$ versus t is extrapolated to the time axis, the resulting intercept, θ is called the time lag.

$$\theta = \frac{l^2}{6D}$$



Time lag measurement of gas permeation

- Instead of measuring a flow, the increment of the permeate pressure (P_2) can be monitored as well. In this way the time-lag can be obtained from a P_2 versus time plot.
- The time-lag method is very suitable for studying ideal systems with a constant diffusion coefficient.
- The permeability coefficient P can be obtained from the steady-state part of this permeation experiment, $\boldsymbol{P = D \cdot S}$, which means that both the diffusion coefficient and the permeability coefficient can be determined from one experiment.
- More complex relationships for the time- lag must be used in concentration dependant system.

Determination of the solubility coefficient

- Once the diffusion coefficient *D* and the permeability coefficient *P* have been determined the solubility coefficient is known as well from the ratio *P/D*.
- Various techniques can be employed to determine the solubility coefficient directly.
- A polymer sample has been applied in a closed, constant volume.
- The volume has been evacuated for a certain period to remove interfering molecules and then a gas is applied at a certain pressure.
- Due to sorption of the gas in the polymer, the pressure decreases in time until equilibrium has been reached and the amount of penetrant inside polymer can now be calculated.

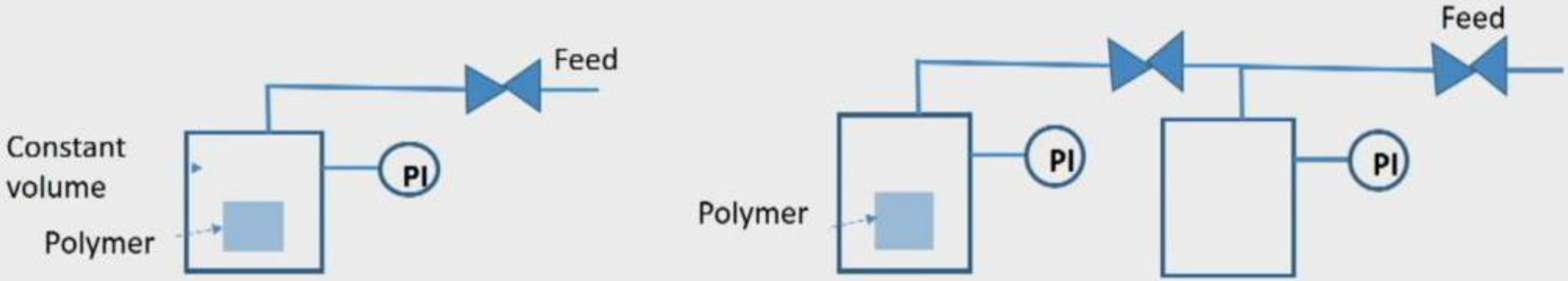


Fig. Schematic drawing of a single volume and a dual volume pressure decay set up

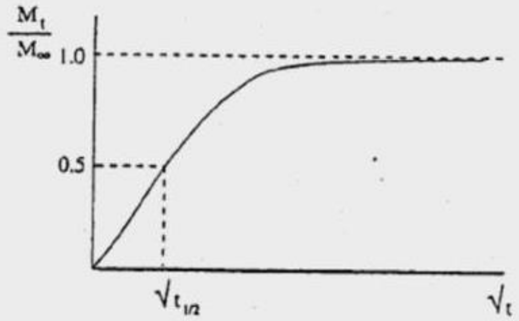


Fig. Sorption isotherm or relative mass uptake versus time

- From the sorption experiments, an effective diffusion coefficient can be determined as well.
- By plotting the ratio of mass uptake at time t (M_t) over the mass uptake at infinite time (M) versus the square root of time, the diffusion coefficient can be obtained from the slope according to the below Eq.

$$\frac{M_t}{M_\infty} = \frac{4}{\sqrt{\pi}}\sqrt{\frac{Dt}{l^2}} \qquad \text{or} \qquad D = \frac{0.049}{t_{1/2}/l^2}$$

- The solution-diffusion model applies to reverse osmosis, pervaporation, and gas permeation in polymer films.
- At first glance, these processes appear to be very different.
- Reverse osmosis uses a large pressure difference across the membrane to separate water from salt solutions.
- In pervaporation, the membrane separates a liquid feed solution from a permeate vapor.
- The pressure difference across the membrane is small, and the process is driven by the vapor pressure difference between the feed liquid and the low partial pressure of the permeate vapor.
- Gas permeation involves transport of gases down a pressure or concentration gradient.
- All three processes involve diffusion of molecules in a dense polymer.

- The pressure, temperature, and composition of the fluids on either side of the membrane determine the concentration of the diffusing species at the membrane surface in equilibrium with the fluid.
- Once dissolved in the membrane, individual permeating molecules move by the same process of random molecular diffusion, no matter whether the membrane is being used in reverse osmosis, pervaporation, or gas permeation.

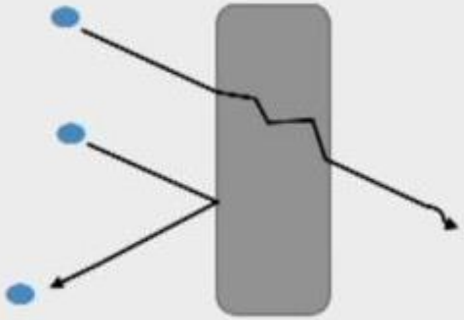
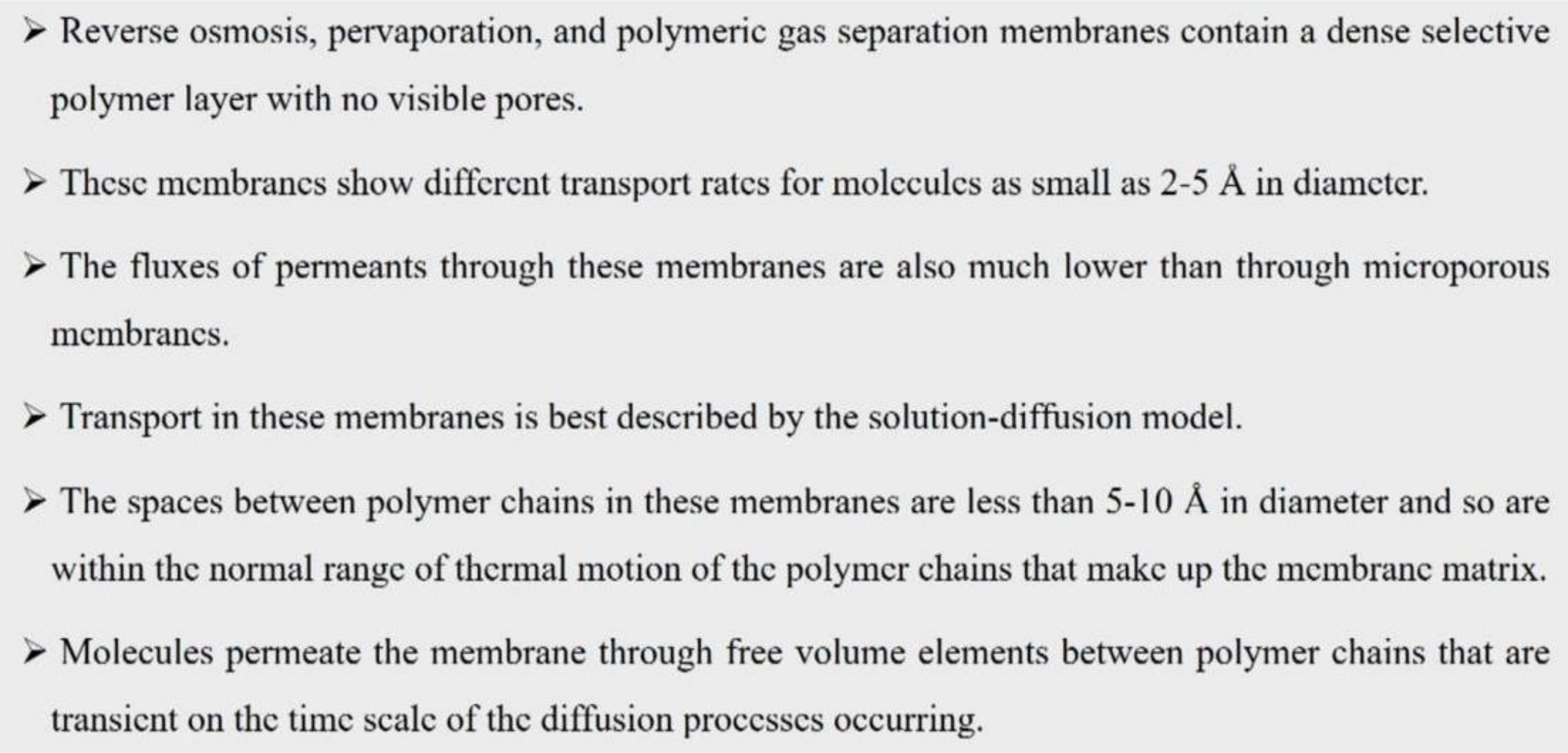


Fig. Dense solution-diffusion membranes separate because of difference in the solubility and mobility of permeates dissolved in the membrane material

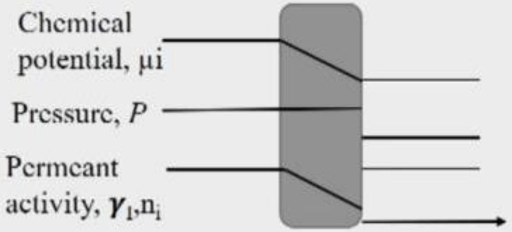


- Reverse osmosis, pervaporation, and polymeric gas separation membranes contain a dense selective polymer layer with no visible pores.
- These membranes show different transport rates for molecules as small as 2-5 Å in diameter.
- The fluxes of permeants through these membranes are also much lower than through microporous membranes.
- Transport in these membranes is best described by the solution-diffusion model.
- The spaces between polymer chains in these membranes are less than 5-10 Å in diameter and so are within the normal range of thermal motion of the polymer chains that make up the membrane matrix.
- Molecules permeate the membrane through free volume elements between polymer chains that are transient on the time scale of the diffusion processes occurring.

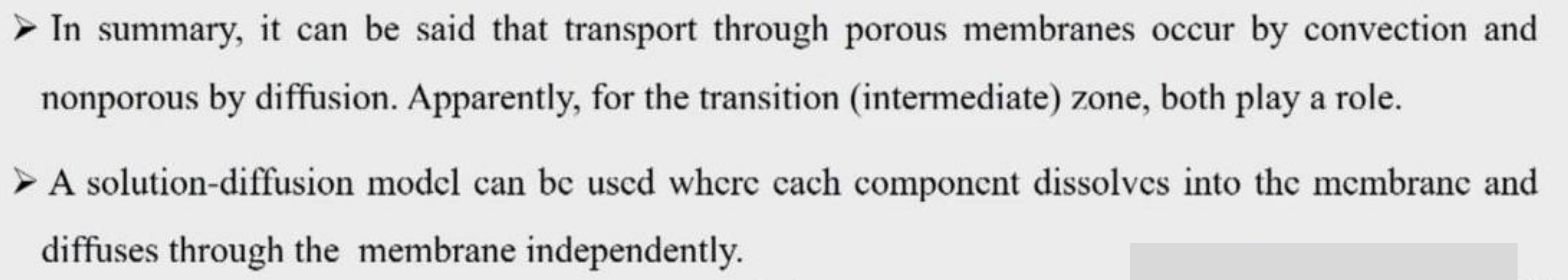
- Membranes in the third group contain pores with diameters between 5 and 15 Å and are intermediate between truly microporous and truly solution-diffusion membranes.
- For example, **nanofiltration membranes** are intermediate between ultrafiltration membranes - *clearly microporous* and reverse osmosis membranes - *clearly dense films*.
- Nanofiltration membranes have high rejections for the di- and trisaccharide's, sucrose and raffinose, with molecular diameters of 10-13 Å, but freely pass the monosaccharide fructose with a molecular diameter of about 5-6 Å.

- Some gas separation membranes also fall into this intermediate category.
- Permeation through dense nonporous membranes includes permeation in reverse osmosis, pervaporation, and gas separation membranes.
- The predictions of this model are in good agreement with experimental data, and a number of simple equations that usefully rationalize the properties of these membranes result.

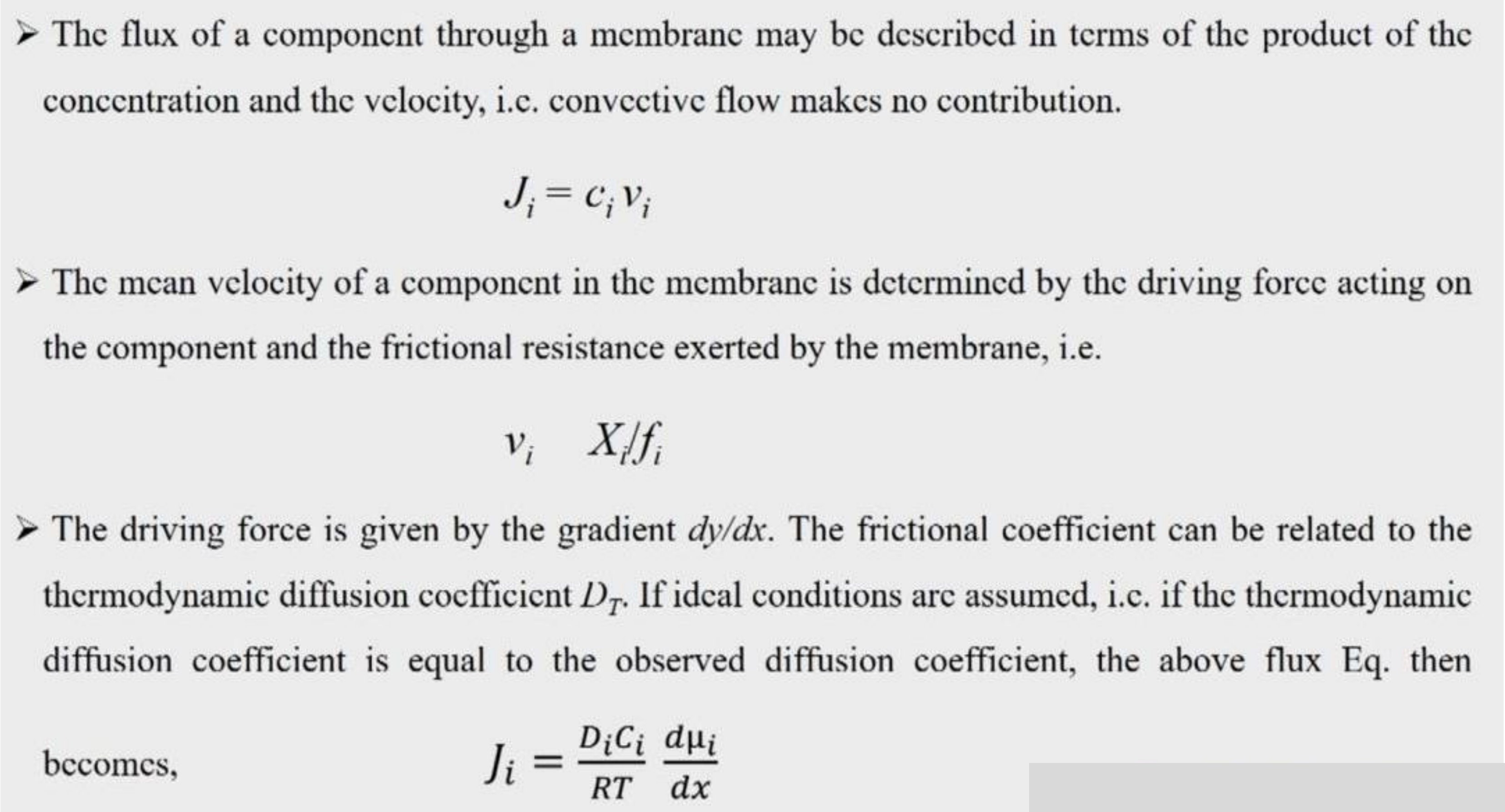
$$\Delta(\gamma_i n_i) = \frac{-V_i(P_o - P_l)}{RT} = \frac{-V_i \Delta\pi}{RT}$$



- $(P_o - P_l) = \Delta\pi$, pressure difference, across the membrane solvent activity difference $\Delta(\gamma_i n_i)$.



- In summary, it can be said that transport through porous membranes occur by convection and nonporous by diffusion. Apparently, for the transition (intermediate) zone, both play a role.
- A solution-diffusion model can be used where each component dissolves into the membrane and diffuses through the membrane independently.



- The flux of a component through a membrane may be described in terms of the product of the concentration and the velocity, i.e. convective flow makes no contribution.

$$J_i = c_i v_i$$

- The mean velocity of a component in the membrane is determined by the driving force acting on the component and the frictional resistance exerted by the membrane, i.e.

$$v_i \quad X_i/f_i$$

- The driving force is given by the gradient *dy/dx*. The frictional coefficient can be related to the thermodynamic diffusion coefficient D_T. If ideal conditions are assumed, i.e. if the thermodynamic diffusion coefficient is equal to the observed diffusion coefficient, the above flux Eq. then becomes,

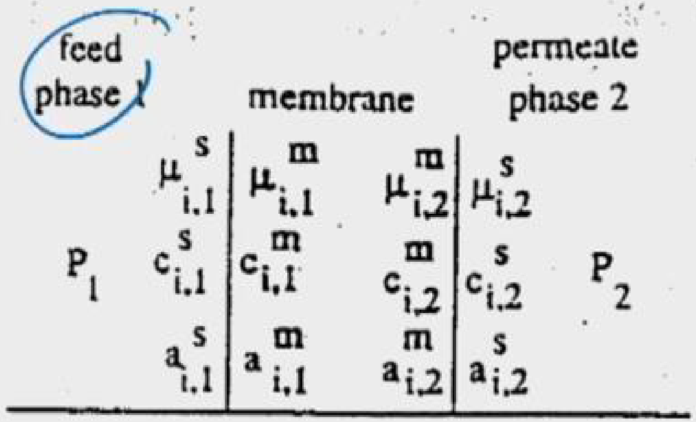
$$J_i = \frac{D_i C_i}{RT} \frac{d\mu_i}{dx}$$

The chemical potential can be written as,

$$\mu_i = \mu_i^o + RT\ \ln a_i + V_i(p - p^0)$$

Substitution in the earlier Eq. yields,

$$J_i = \frac{D_i c_i}{RT}\left[RT\ \frac{d\ln a_i}{dx} + V_i \frac{dP}{dx}\ \right]$$

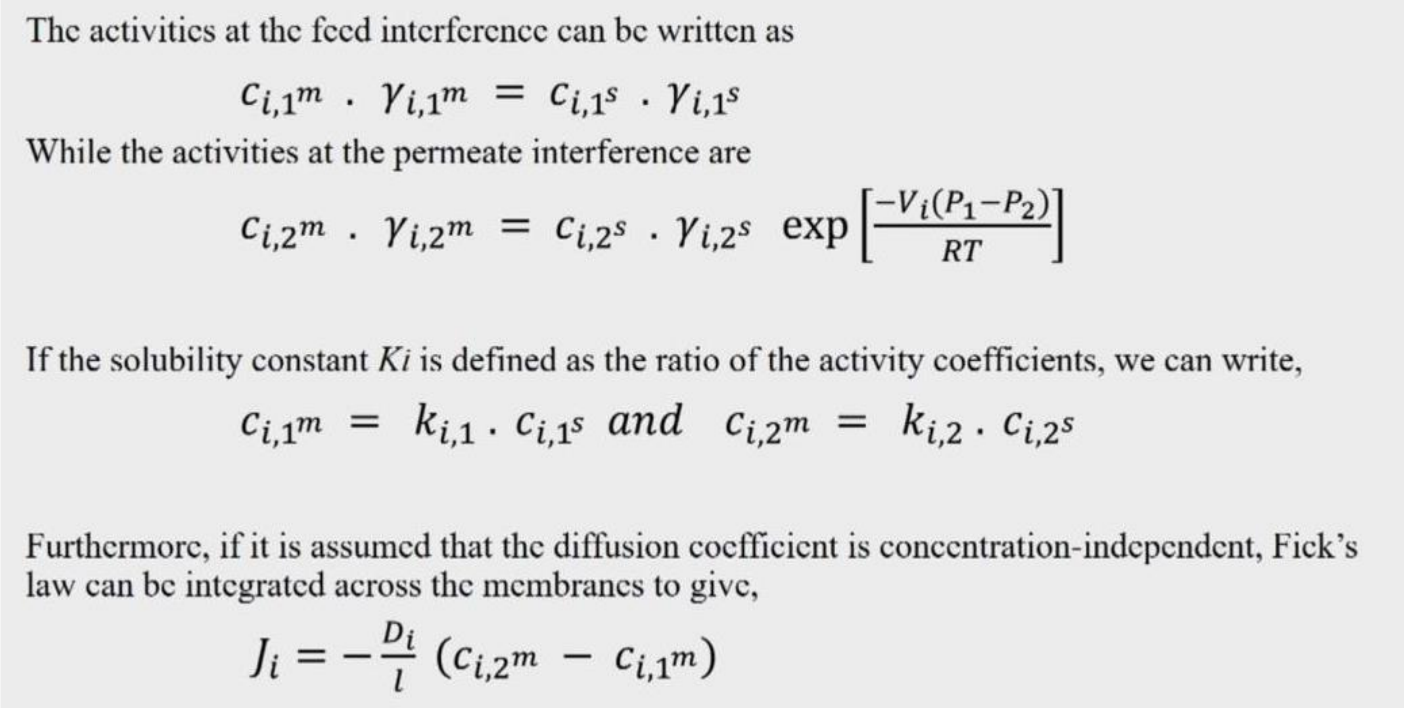


At the feed interference (phase 1 membrane)

$$\mu_{i,1^m} = \mu_{i,1^s} \rightarrow a_{i,1^m}\ = a_{i,1^s}$$

And at the permeate interference (phase 2 membrane)

$$\mu_{i,2^m} = \mu_{i,2^s} \rightarrow a_{i,2^m} = a_{i,2^s}\ \exp\left[\frac{-V_i(P_1 - P_2)}{RT}\right]$$



The activities at the feed interference can be written as

$$c_{i,1^m}\ .\ \gamma_{i,1^m} = c_{i,1^s}\ .\ \gamma_{i,1^s}$$

While the activities at the permeate interference are

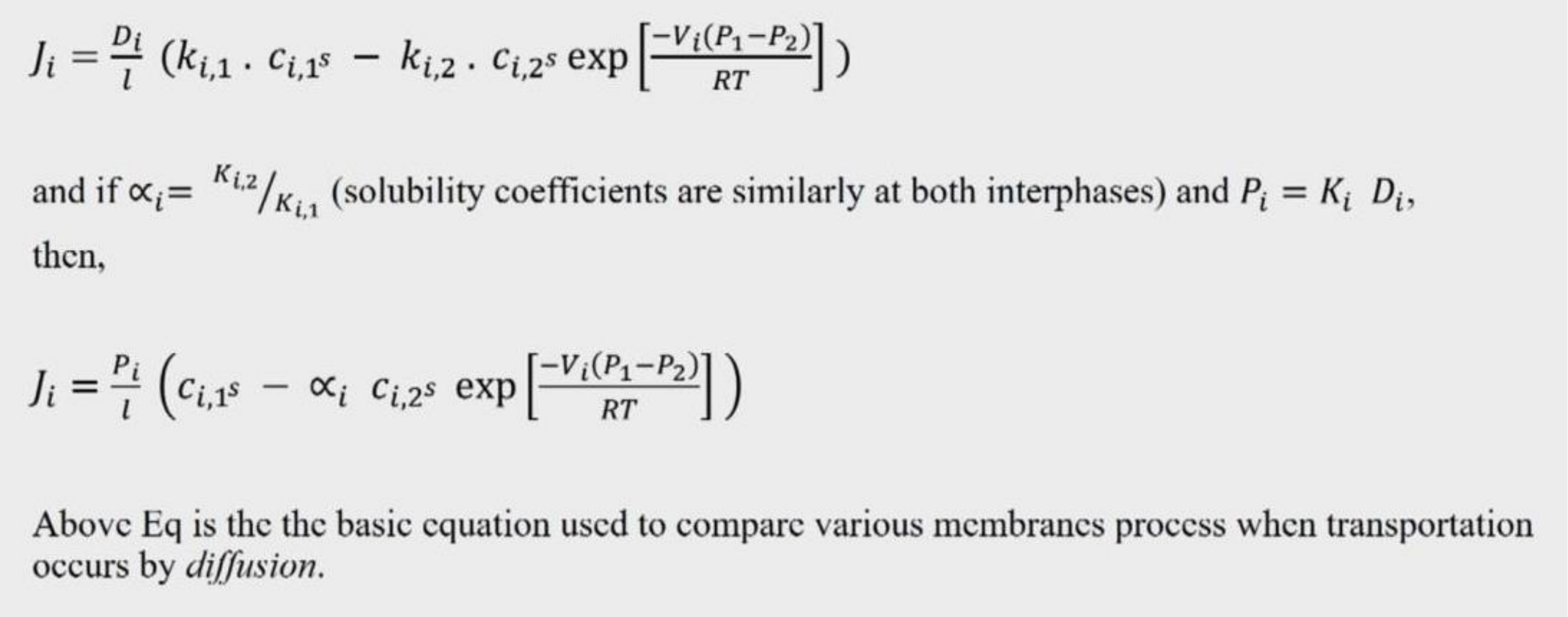
$$c_{i,2^m}\ .\ \gamma_{i,2^m} = c_{i,2^s}\ .\ \gamma_{i,2^s}\ \exp\left[\frac{-V_i(P_1-P_2)}{RT}\right]$$

If the solubility constant *Ki* is defined as the ratio of the activity coefficients, we can write,

$$c_{i,1^m} = k_{i,1}\,.\,c_{i,1^s}\ \mathit{and}\ \ c_{i,2^m} = k_{i,2}\,.\,c_{i,2^s}$$

Furthermore, if it is assumed that the diffusion coefficient is concentration-independent, Fick's law can be integrated across the membranes to give,

$$J_i = -\frac{D_i}{l}\left(c_{i,2^m} - c_{i,1^m}\right)$$



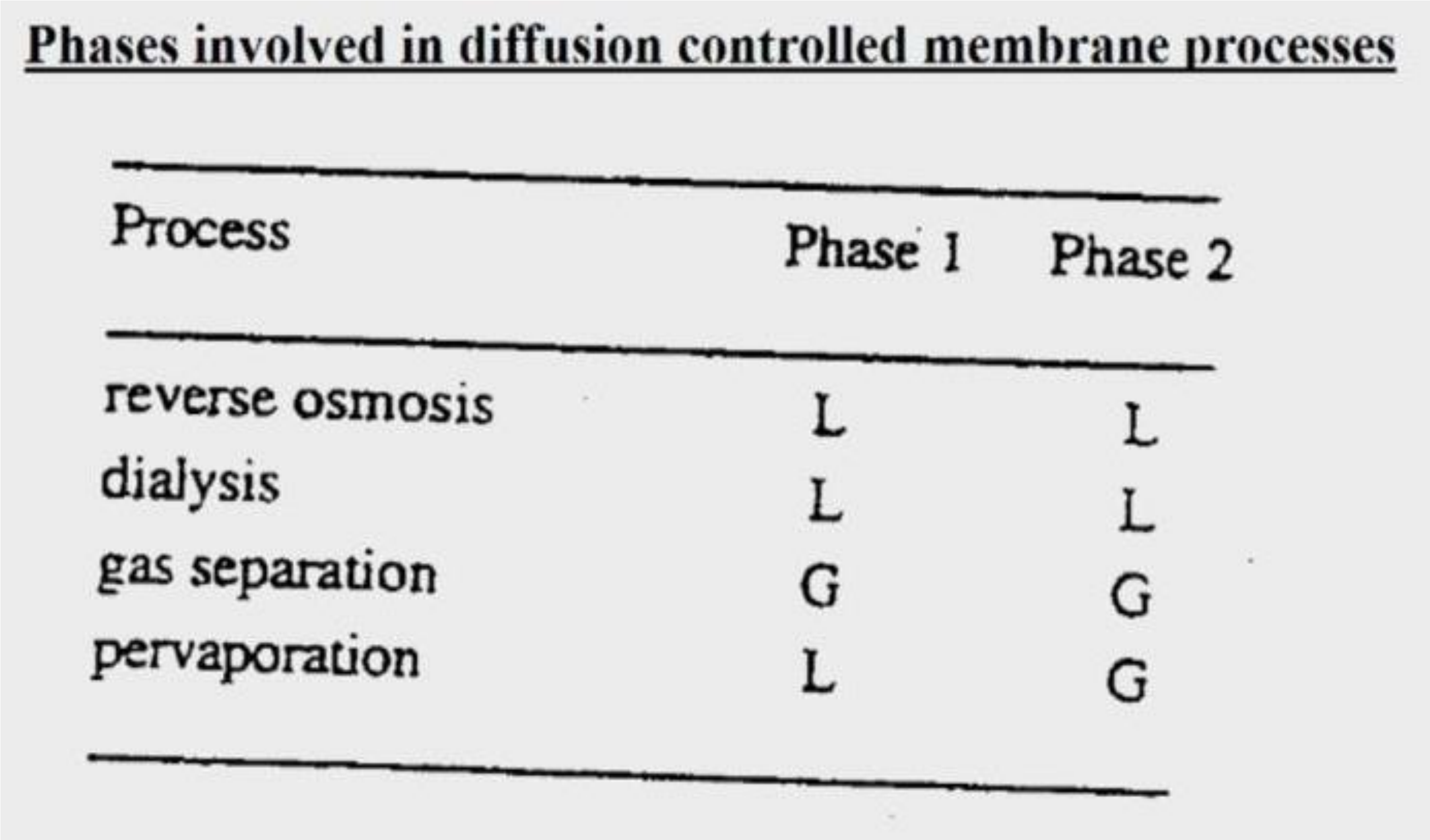
$$J_i = \frac{D_i}{l}\left(k_{i,1}\,.\,c_{i,1^s} - k_{i,2}\,.\,c_{i,2^s}\exp\left[\frac{-V_i(P_1-P_2)}{RT}\right]\right)$$

and if $\propto_i = {}^{K_{i,2}}/_{K_{i,1}}$ (solubility coefficients are similarly at both interphases) and $P_i = K_i\ D_i$,

then,

$$J_i = \frac{P_i}{l}\left(c_{i,1^s} - \propto_i\ c_{i,2^s}\ \exp\left[\frac{-V_i(P_1-P_2)}{RT}\right]\right)$$

Above Eq is the the basic equation used to compare various membranes process when transportation occurs by *diffusion*.

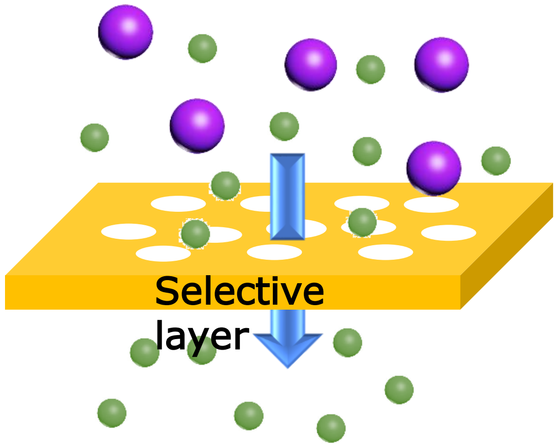


Phases involved in diffusion controlled membrane processes

Process	Phase 1	Phase 2
reverse osmosis	L	L
dialysis	L	L
gas separation	G	G
pervaporation	L	G

PROSES PEMISAHAN

Ultrafitration (UF)

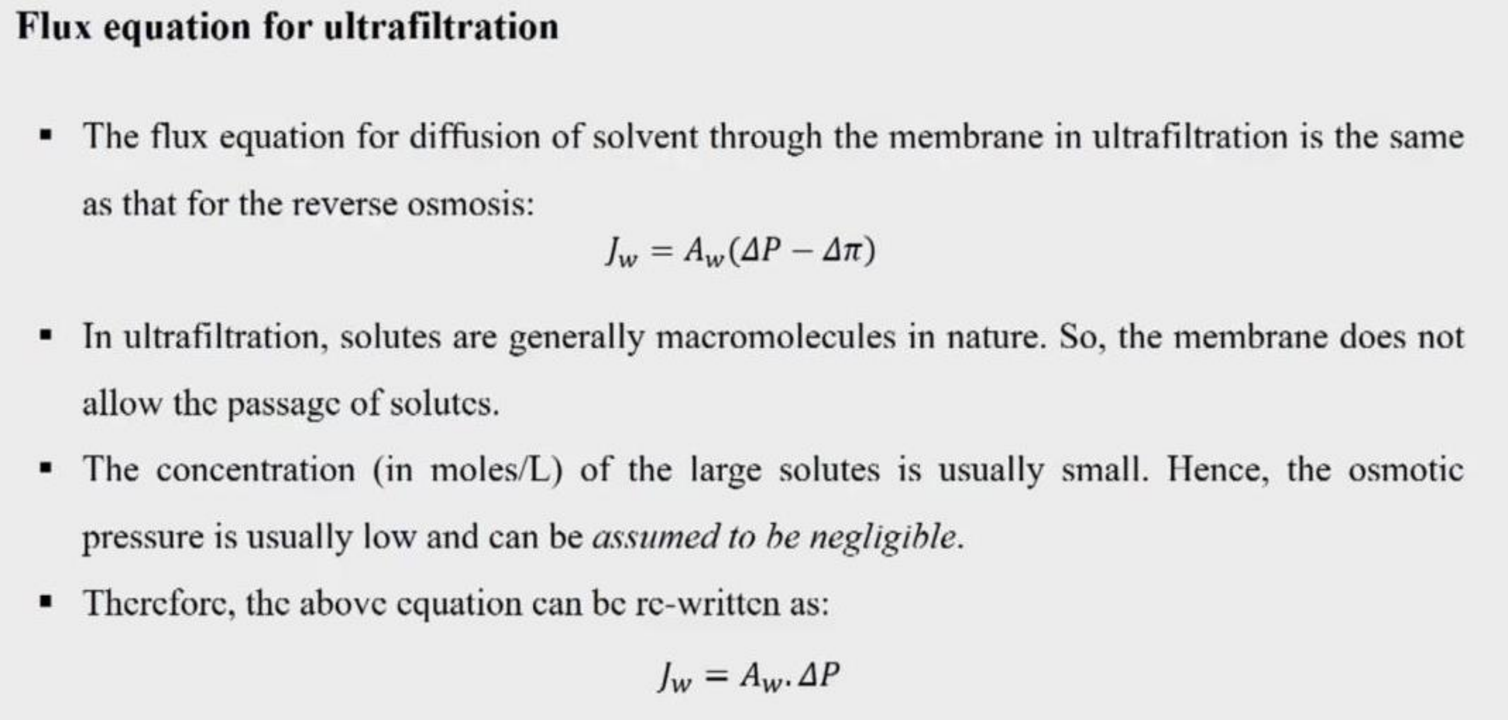


Oleh : Indah Prihatiningtyas D.S

Ultrafiltration (UF)

size: 0.01 to 1 micron

MW: 10^3 to 10^6 Dalton



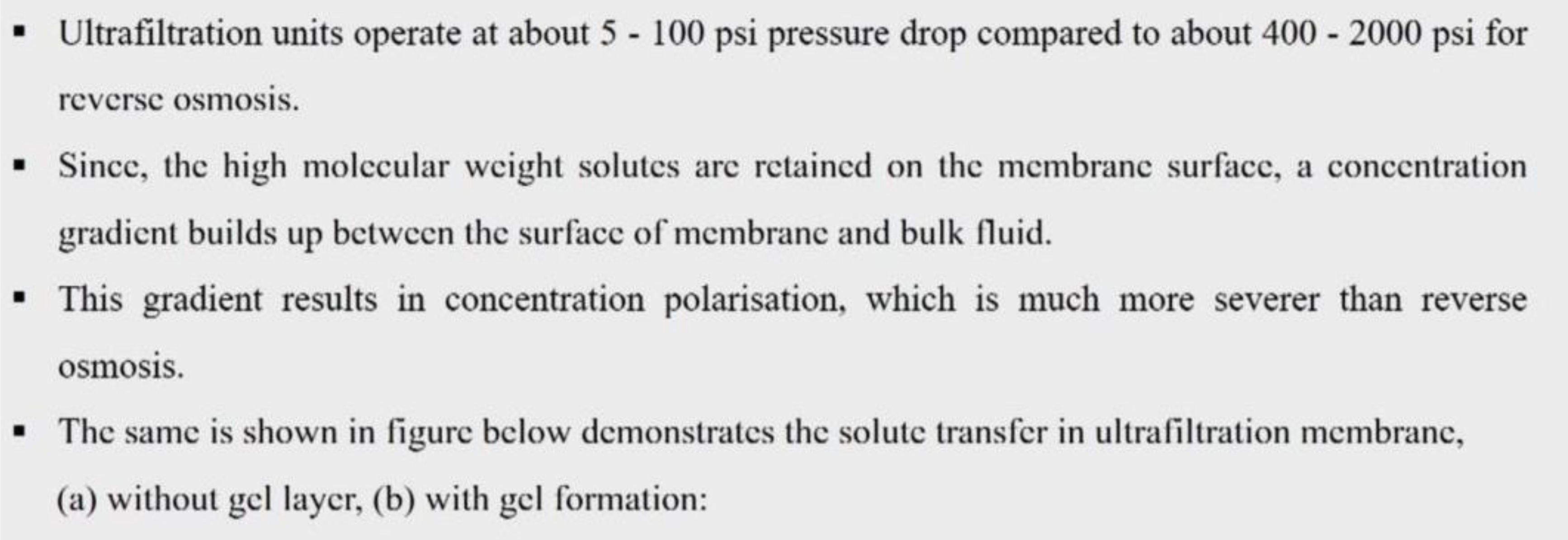
Flux equation for ultrafiltration

- The flux equation for diffusion of solvent through the membrane in ultrafiltration is the same as that for the reverse osmosis:

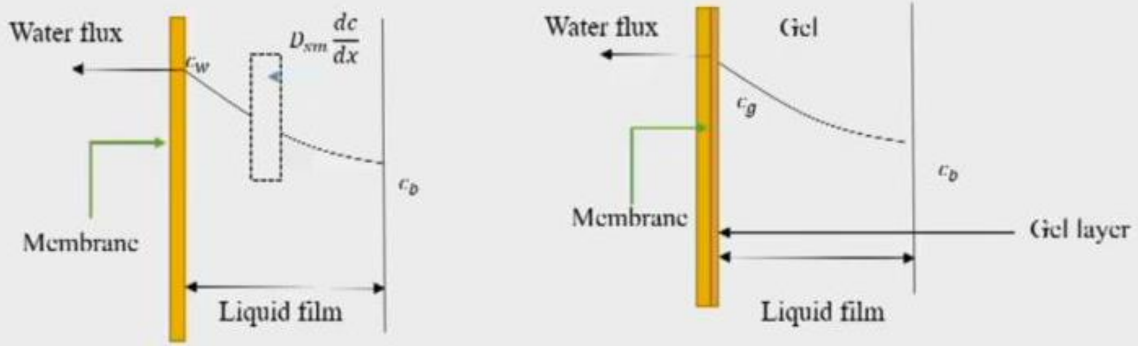
$$J_w = A_w(\Delta P - \Delta\pi)$$

- In ultrafiltration, solutes are generally macromolecules in nature. So, the membrane does not allow the passage of solutes.
- The concentration (in moles/L) of the large solutes is usually small. Hence, the osmotic pressure is usually low and can be *assumed to be negligible*.
- Therefore, the above equation can be re-written as:

$$J_w = A_w . \Delta P$$



- Ultrafiltration units operate at about 5 - 100 psi pressure drop compared to about 400 - 2000 psi for reverse osmosis.
- Since, the high molecular weight solutes are retained on the membrane surface, a concentration gradient builds up between the surface of membrane and bulk fluid.
- This gradient results in concentration polarisation, which is much more severer than reverse osmosis.
- The same is shown in figure below demonstrates the solute transfer in ultrafiltration membrane, (a) without gel layer, (b) with gel formation:



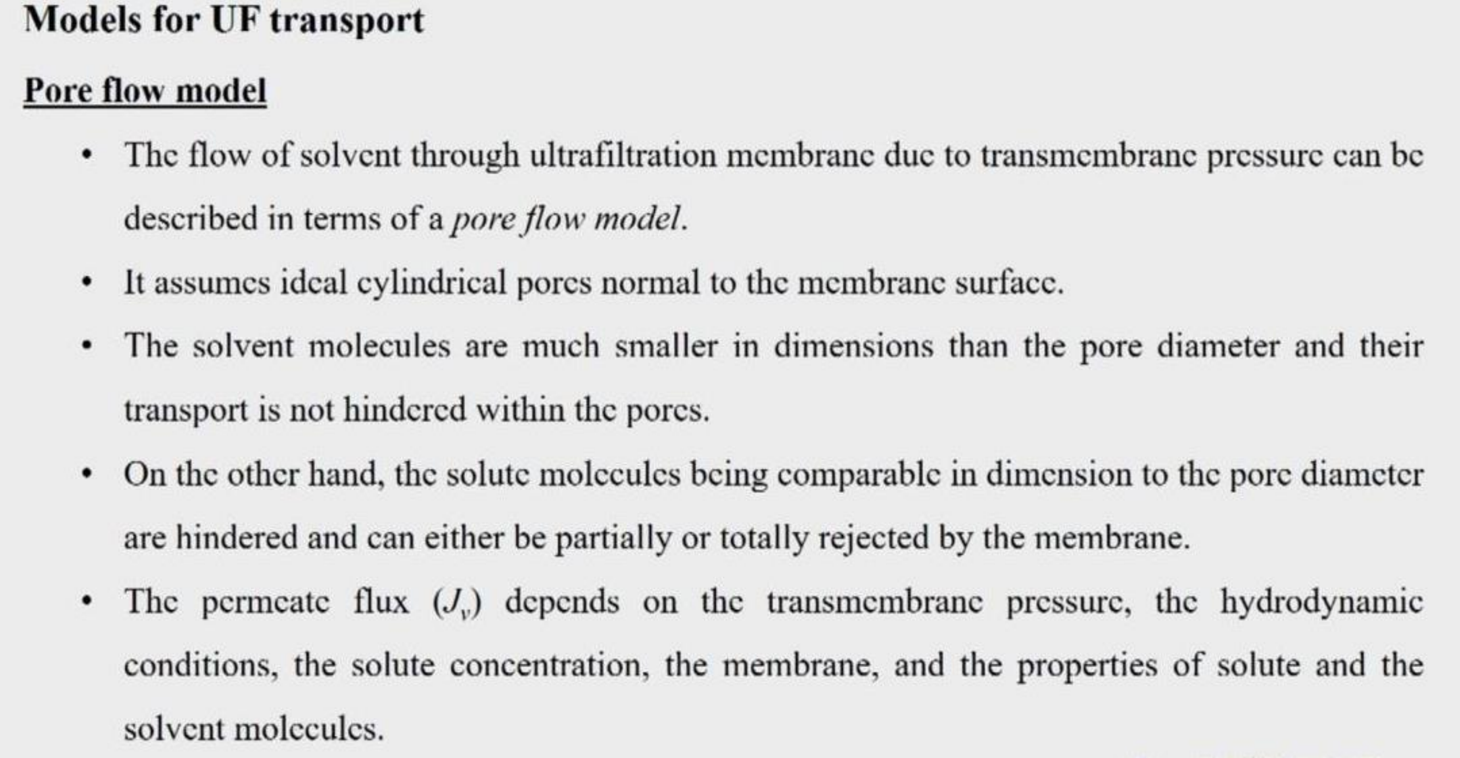
(a) without gel layer (b) with gel formation

where, D_{sm} is the diffusivity of solute in membrane, J_w is volumetric flux of liquids, and c is the concentration of solute.

- Still further increase in pressure drop does not change c_g and the membrane is said to be gel polarised.
- Then, the above equation becomes:

$$J_w = k_c \ln\frac{c_g}{c_b}$$

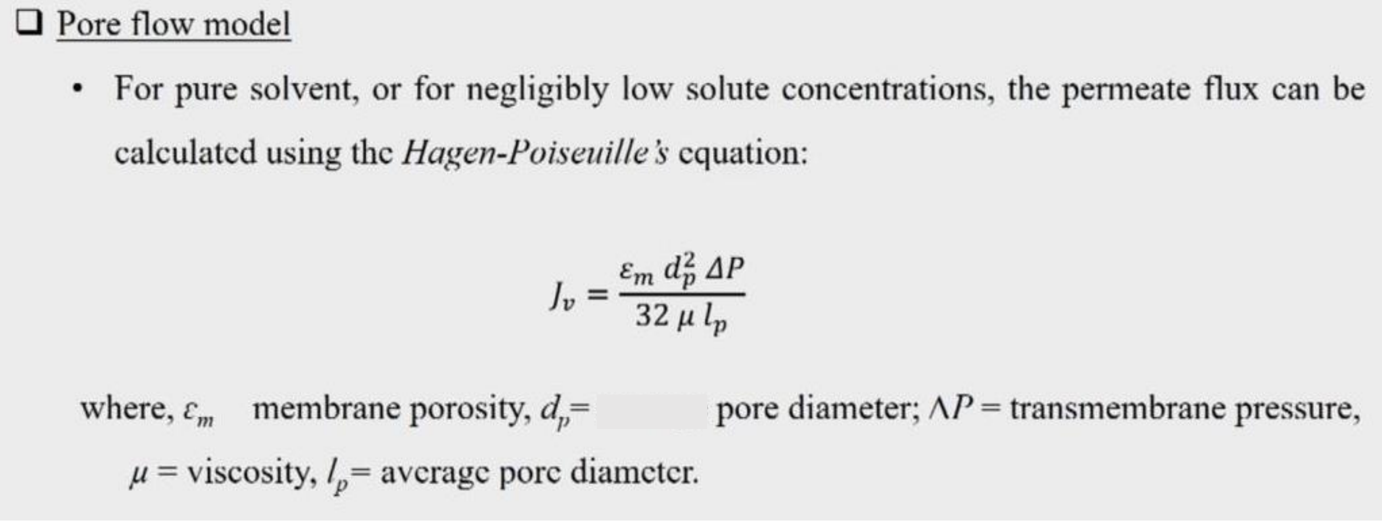
- Gel formation depends on the nature and concentration of the solute, pH, and pressure. Once the gel is formed, c_g becomes constant, and the liquid flux decreases logarithmically with increasing solute concentration in the bulk liquid.
- The gel layer causes a hydraulic resistance against flow and acts somewhat like a second membrane.



Models for UF transport

Pore flow model

- The flow of solvent through ultrafiltration membrane due to transmembrane pressure can be described in terms of a *pore flow model*.
- It assumes ideal cylindrical pores normal to the membrane surface.
- The solvent molecules are much smaller in dimensions than the pore diameter and their transport is not hindered within the pores.
- On the other hand, the solute molecules being comparable in dimension to the pore diameter are hindered and can either be partially or totally rejected by the membrane.
- The permeate flux (J_v) depends on the transmembrane pressure, the hydrodynamic conditions, the solute concentration, the membrane, and the properties of solute and the solvent molecules.



❑ Pore flow model

- For pure solvent, or for negligibly low solute concentrations, the permeate flux can be calculated using the *Hagen-Poiseuille's* equation:

$$J_v = \frac{\varepsilon_m \, d_p^2 \, \Delta P}{32 \, \mu \, l_p}$$

where, ε_m membrane porosity, d_p= pore diameter; ΛP = transmembrane pressure, μ = viscosity, l_p= average pore diameter.

Pore flow model

- The above equation shows that the permeate flux is very sensitive to the pore diameter.
- The permeate flux also increases with increase in trans-membrane pressure and the membrane porosity.
- On the other hand, the permeate flux decreases with increase in viscosity and membrane thickness.
- The pressure drop of membrane module is given by:

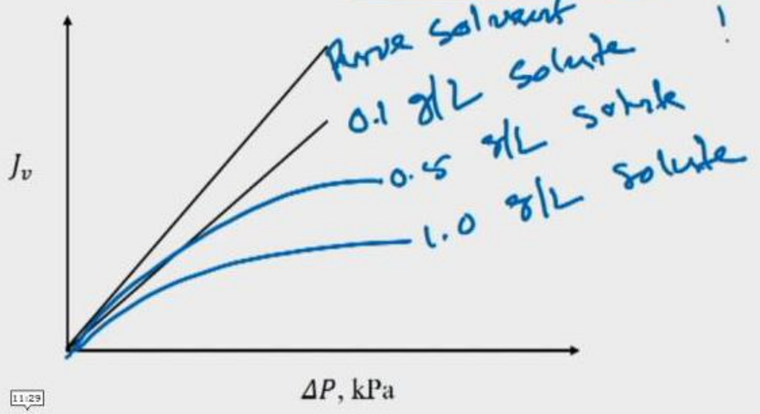
$$\Delta P = \frac{P_i + P_o}{2} - P_f$$

where, P_i and P_o are the inlet and outlet pressure on the feed side and P_f is the pressure on the filtrate side.

Models for UF transport

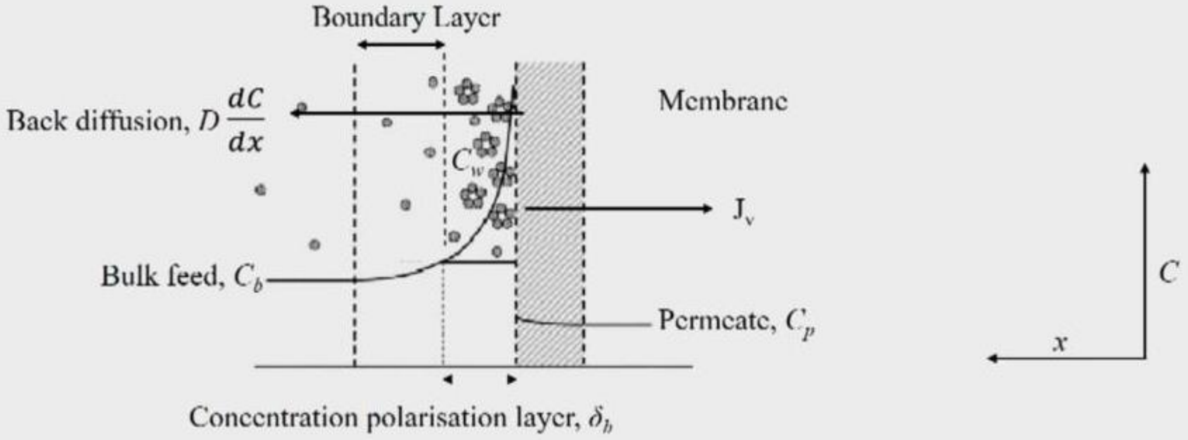
☐ Concentration polarization model

- It is observed that the permeate flux in an ultrafiltration process does not increases linearly with transmembrane pressure after a certain point.
- This is due to the build up of rejected solute molecules near the membrane surface and this phenomenon is referred to as concentration polarization.



☐ Concentration polarization model

- The concentration profile of solute molecules closed to the membrane surface is shown in figure below:



❑ Concentration polarization model

- At steady state, a material balance of solute molecules in a control volume within the concentration polarization layer yields the following differential equation:

$$J_v C - J_v C_p + D\frac{dC}{dx} = 0$$

- Integrating the above equation with boundary conditions, $C = C_w$ at $x = 0$; $C = C_b$ at $x = \delta_b$, we get:

$$J_v = k\ln\left(\frac{C_w - C_p}{C_b - Cp}\right)$$

since, mass transfer coefficient, $k = D/\ \delta_b$.

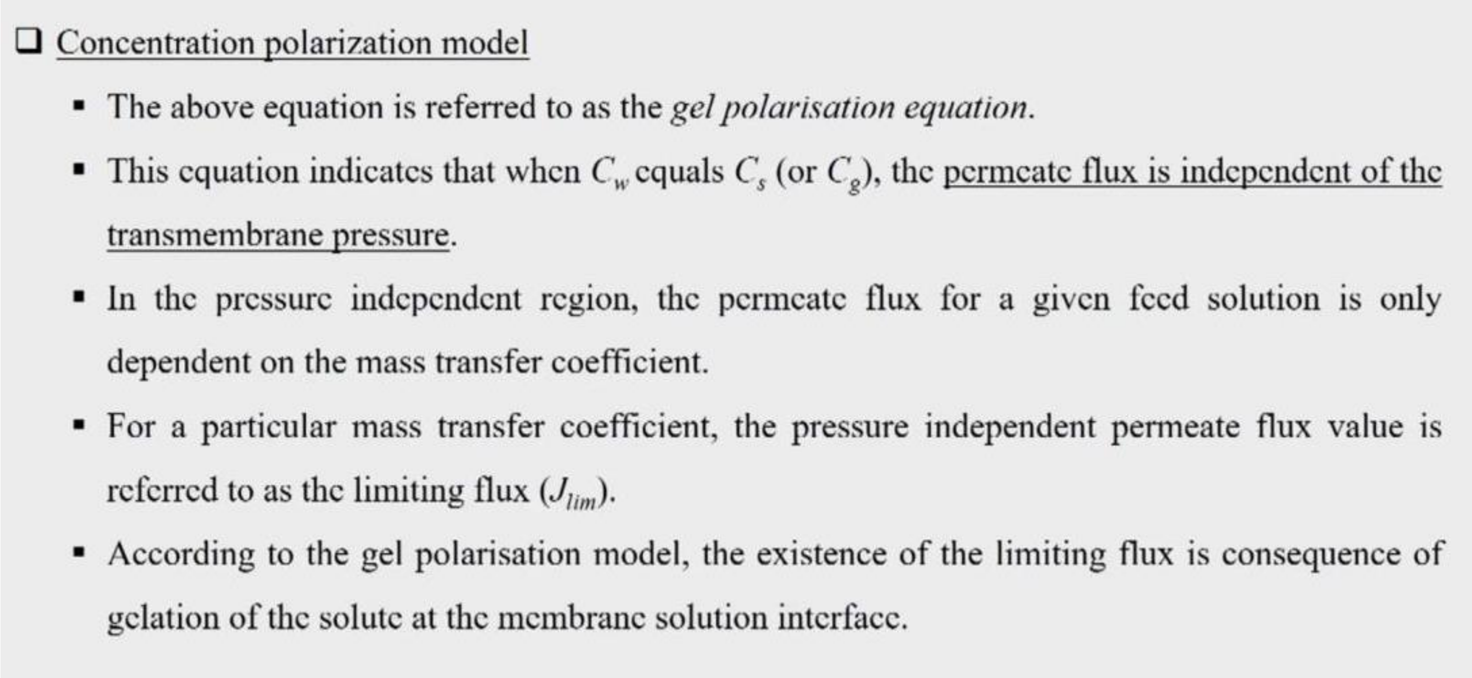
❑ Concentration polarization model

- The above equation is known as the *concentration polarisation equation for partially rejected solutes*. For total solute rejection, i.e. when $C_p = 0$, the equation reduces to:

$$J_v = k\ln\left(\frac{C_w}{C_b}\right)$$

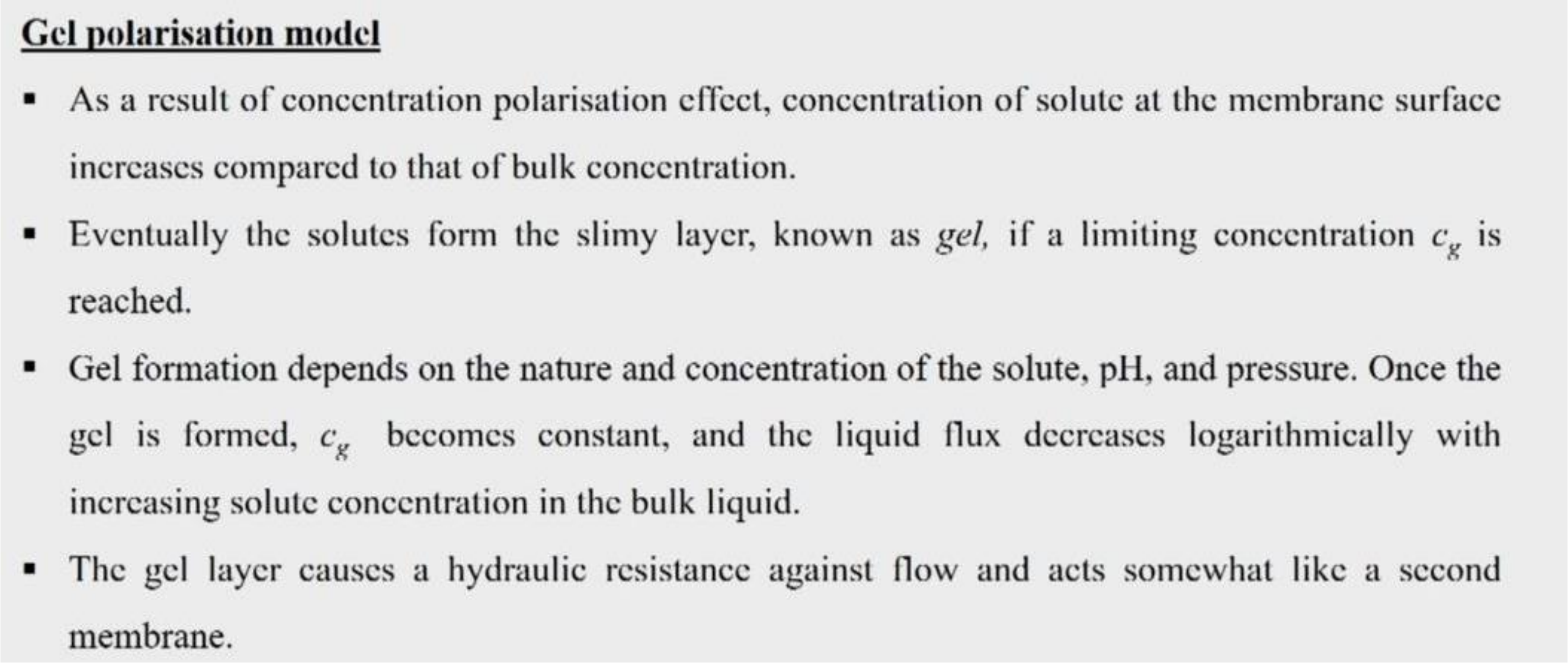
- When the solute concentration at the membrane surface reaches the saturation concentration for the solute (C_s), or the gelation concentration at the macromolecule (C_g), there can be no further increase in C_w. Thus,

$$J_v = k\ln\left(\frac{C_s}{C_b}\right) = k\ln\left(\frac{C_g}{C_b}\right)$$



☐ Concentration polarization model

- The above equation is referred to as the *gel polarisation equation*.
- This equation indicates that when C_w equals C_s (or C_g), the permeate flux is independent of the transmembrane pressure.
- In the pressure independent region, the permeate flux for a given feed solution is only dependent on the mass transfer coefficient.
- For a particular mass transfer coefficient, the pressure independent permeate flux value is referred to as the limiting flux (J_{lim}).
- According to the gel polarisation model, the existence of the limiting flux is consequence of gelation of the solute at the membrane solution interface.



Gel polarisation model

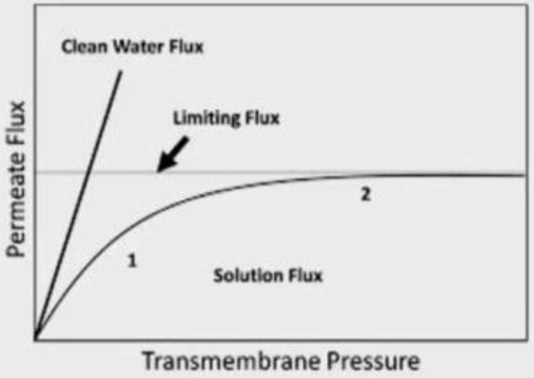
- As a result of concentration polarisation effect, concentration of solute at the membrane surface increases compared to that of bulk concentration.
- Eventually the solutes form the slimy layer, known as *gel,* if a limiting concentration c_g is reached.
- Gel formation depends on the nature and concentration of the solute, pH, and pressure. Once the gel is formed, c_g becomes constant, and the liquid flux decreases logarithmically with increasing solute concentration in the bulk liquid.
- The gel layer causes a hydraulic resistance against flow and acts somewhat like a second membrane.

- At steady state, a constant thickness of the gel and a limiting flux, J_{lim} are attained. If k_c is the mass transfer coefficient, total resistance would be the sum of membrane resistance and gel resistance.
- The equation for limiting flux becomes:

$$J_{\text{lim}} = \frac{\Delta P}{\mu\,(R_m + R_g)} = k_c \ln\left(\frac{C_g - C_p}{C_b - C_p}\right)$$

- If the solute rejection is high (i.e. $c_p << c_b$ and c_s), where, c_p is permeate concentration.

$$J_{\text{lim}} = k_c\,(\ln C_g - \ln C_b)$$



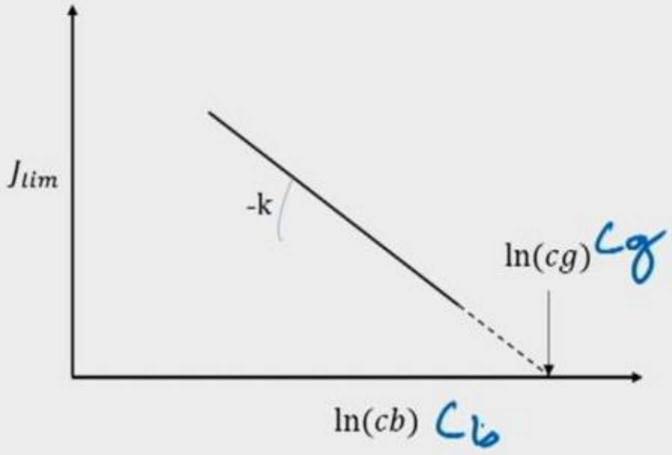
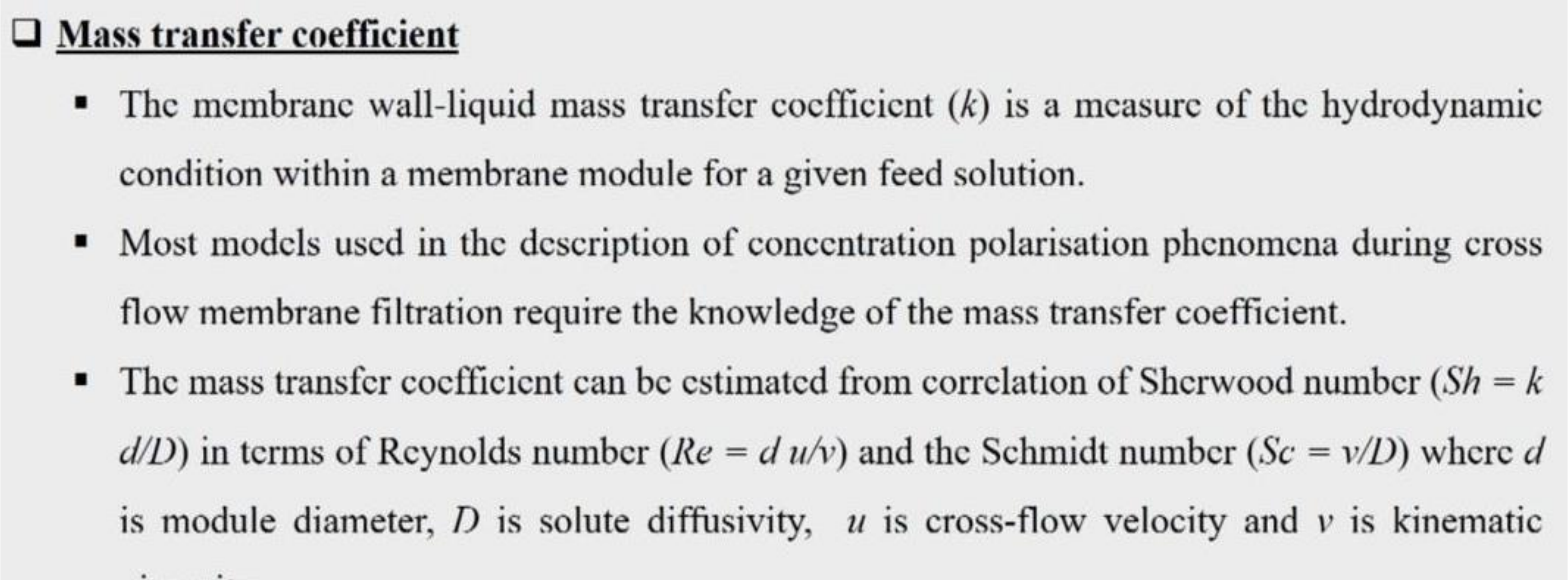


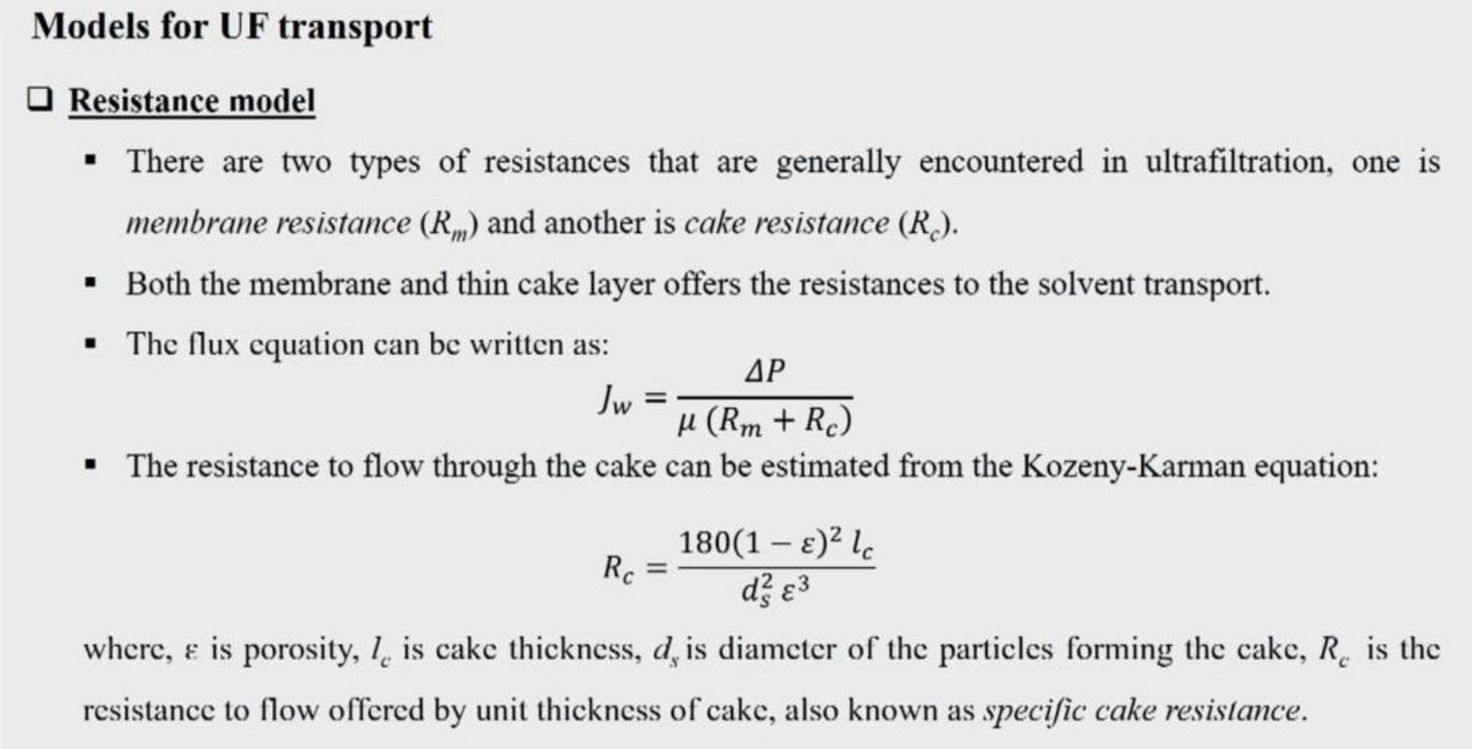
Fig. Limiting flux plotted as a function of the logarithm of the concentration of the bulk feed

- It is assumed that gel concentration remains constant across the gel layer.
- However, in reality, it is not the same as gel concentration depends on bulk concentration and the cross-flow velocity.
- Further, k is assumed as constant, however, the diffusivity of the macromolecular solute is often concentration-dependent.



❑ Mass transfer coefficient

- The membrane wall-liquid mass transfer coefficient (k) is a measure of the hydrodynamic condition within a membrane module for a given feed solution.
- Most models used in the description of concentration polarisation phenomena during cross flow membrane filtration require the knowledge of the mass transfer coefficient.
- The mass transfer coefficient can be estimated from correlation of Sherwood number ($Sh = k\, d/D$) in terms of Reynolds number ($Re = d\, u/v$) and the Schmidt number ($Sc = v/D$) where d is module diameter, D is solute diffusivity, u is cross-flow velocity and v is kinematic viscosity.



Models for UF transport

❑ Resistance model

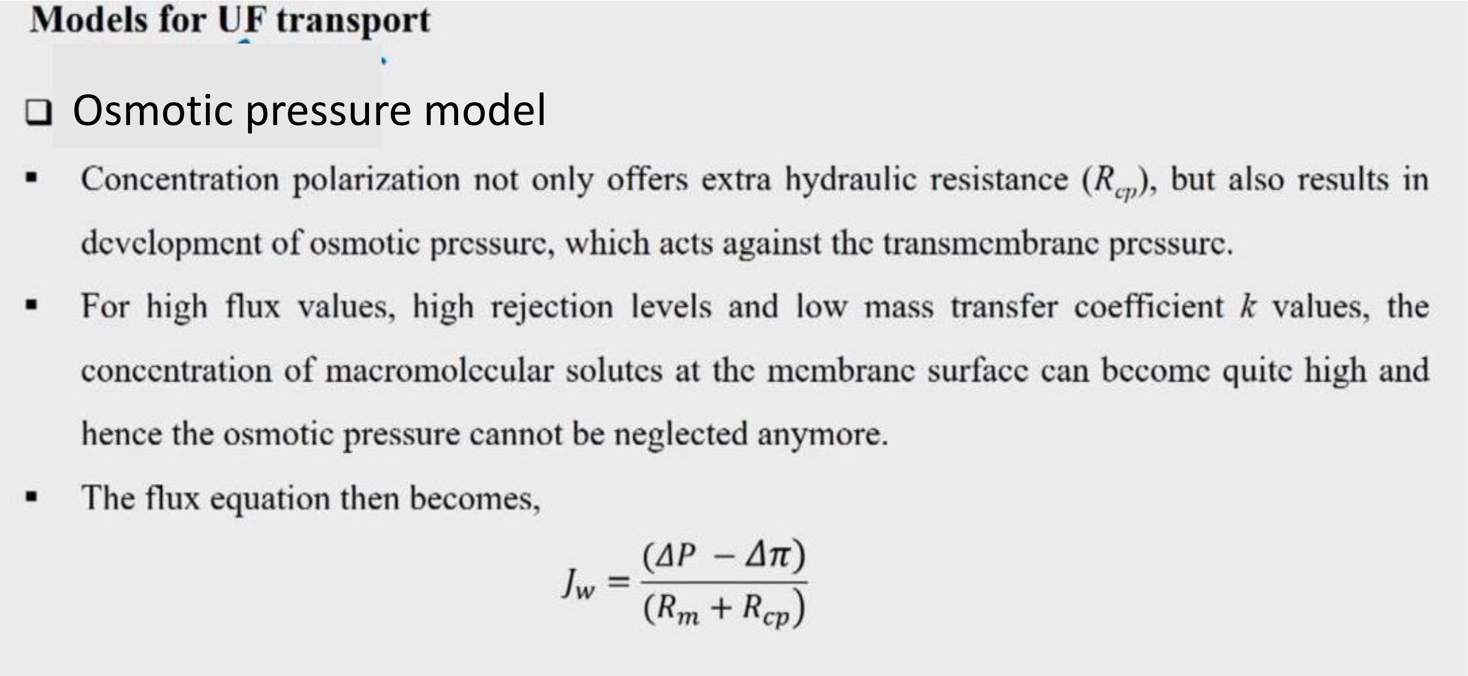
- There are two types of resistances that are generally encountered in ultrafiltration, one is *membrane resistance* (R_m) and another is *cake resistance* (R_c).
- Both the membrane and thin cake layer offers the resistances to the solvent transport.
- The flux equation can be written as:

$$J_w = \frac{\Delta P}{\mu\,(R_m + R_c)}$$

- The resistance to flow through the cake can be estimated from the Kozeny-Karman equation:

$$R_c = \frac{180(1-\varepsilon)^2\, l_c}{d_s^2\, \varepsilon^3}$$

where, ε is porosity, l_c is cake thickness, d_s is diameter of the particles forming the cake, R_c is the resistance to flow offered by unit thickness of cake, also known as *specific cake resistance*.

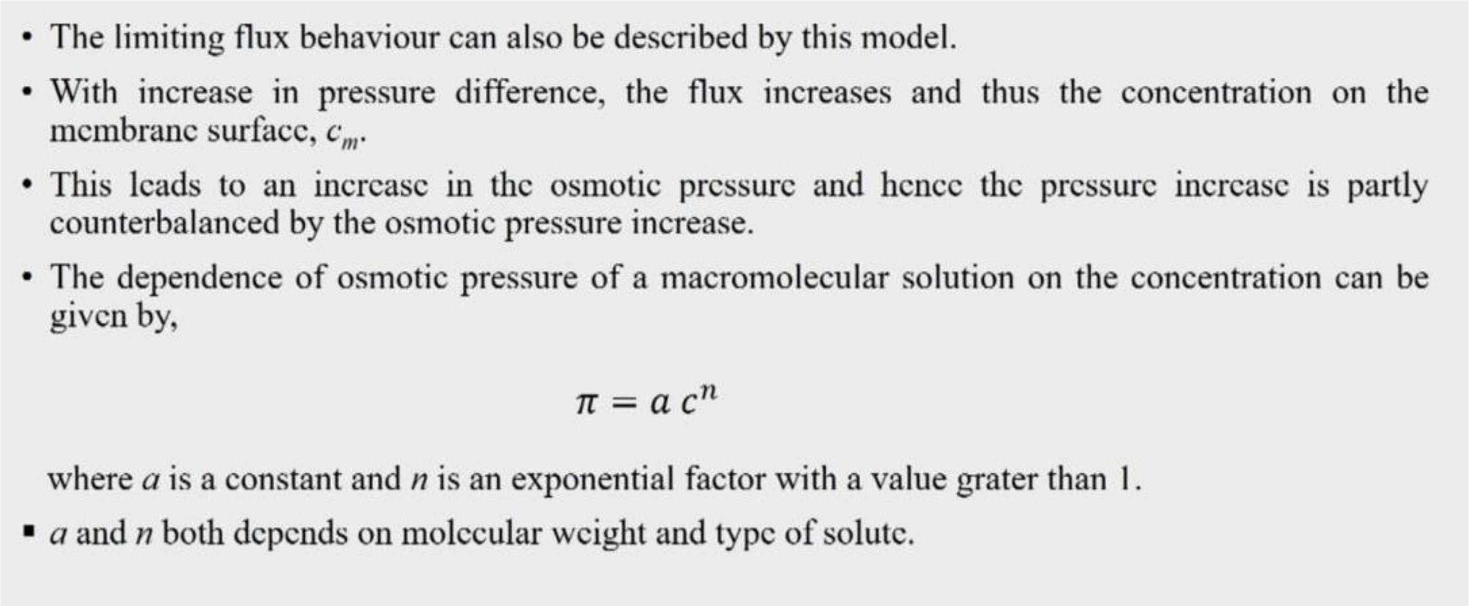


Models for UF transport

❑ Osmotic pressure model

- Concentration polarization not only offers extra hydraulic resistance (R_{cp}), but also results in development of osmotic pressure, which acts against the transmembrane pressure.
- For high flux values, high rejection levels and low mass transfer coefficient k values, the concentration of macromolecular solutes at the membrane surface can become quite high and hence the osmotic pressure cannot be neglected anymore.
- The flux equation then becomes,

$$J_w = \frac{(\Delta P\ - \Delta\pi)}{(R_m + R_{cp})}$$



- The limiting flux behaviour can also be described by this model.
- With increase in pressure difference, the flux increases and thus the concentration on the membrane surface, c_m.
- This leads to an increase in the osmotic pressure and hence the pressure increase is partly counterbalanced by the osmotic pressure increase.
- The dependence of osmotic pressure of a macromolecular solution on the concentration can be given by,

$$\pi = a\, c^n$$

where a is a constant and n is an exponential factor with a value grater than 1.

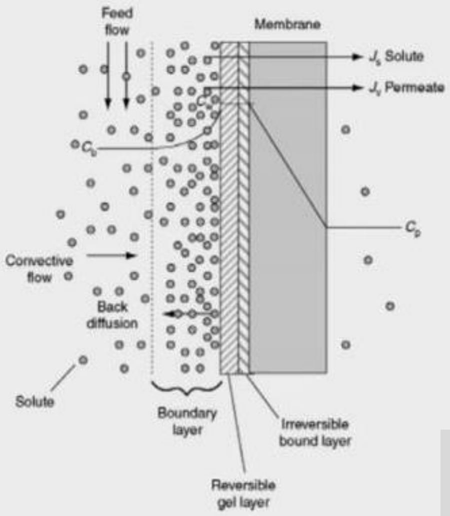
- a and n both depends on molecular weight and type of solute.

❑ **Membrane Rejection**

- The concept of molecular weight cut-off can be arbitrary.
- The consequences of the non-standard protocols, difference in membrane morphology, generic polymer composition, and the chemical nature of the MWCO tests all contribute to this uncertainty.
- The retention properties of the membrane are strongly dependent on the solute shape, solute flexibility, solute-membrane interaction, operating conditions, and the test apparatus configuration.

Enhancement of permeate flux

- As we know that permeate flux depends on the mass transfer coefficient; for a given feed concentration and transmembrane pressure, the higher the value of k, the higher the permeate flux.
- The permeate flux can also be increased by disrupting the concentration polarization layer.
- Some of the techniques are:
  - ➢By increasing the feed flow rate
  - ➢By creating pulsatile flow
  - ➢By pressure pulsing
  - ➢By creating oscillatory flow
  - ➢By flow obstructing using baffles
  - ➢By generating Taylor vortex
  - ➢By gas-sparging



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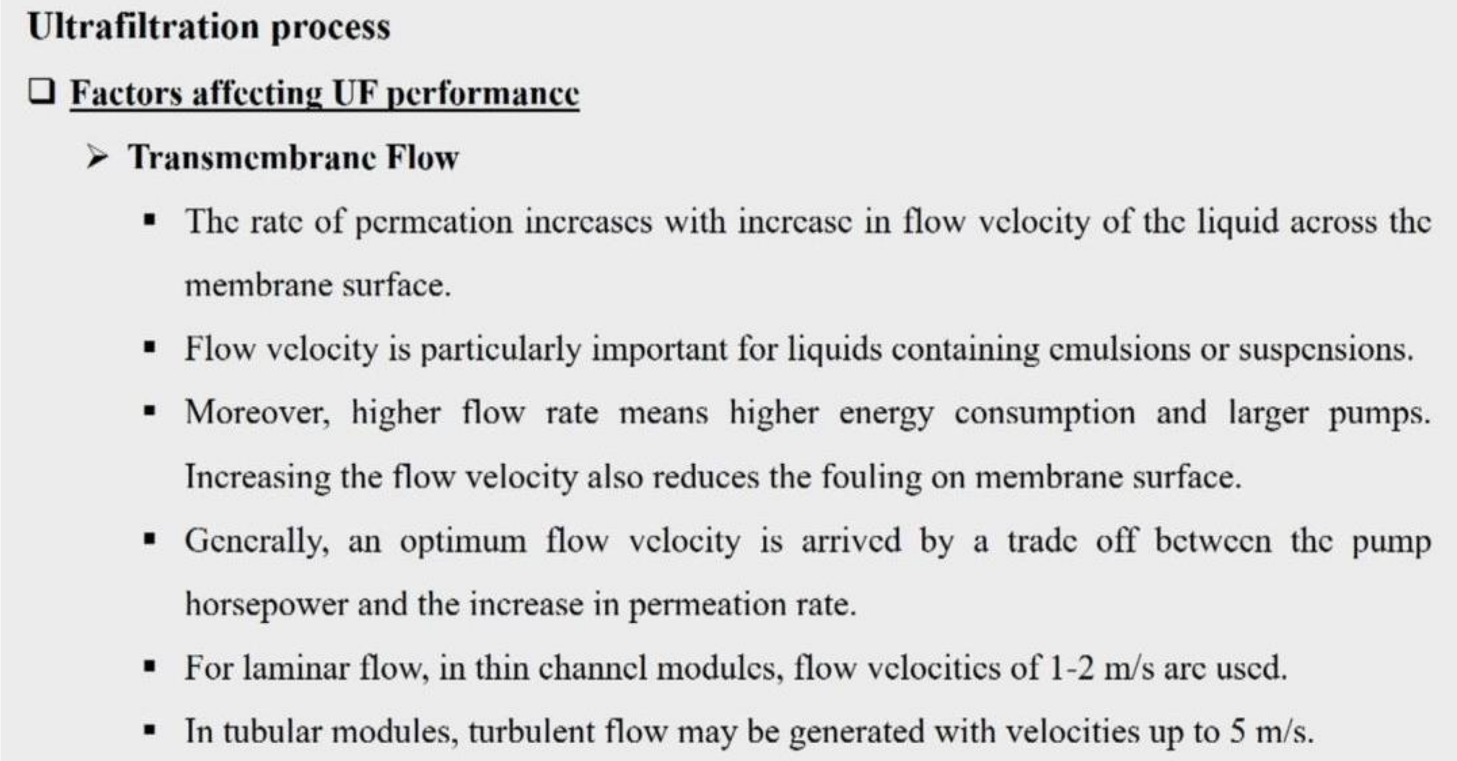
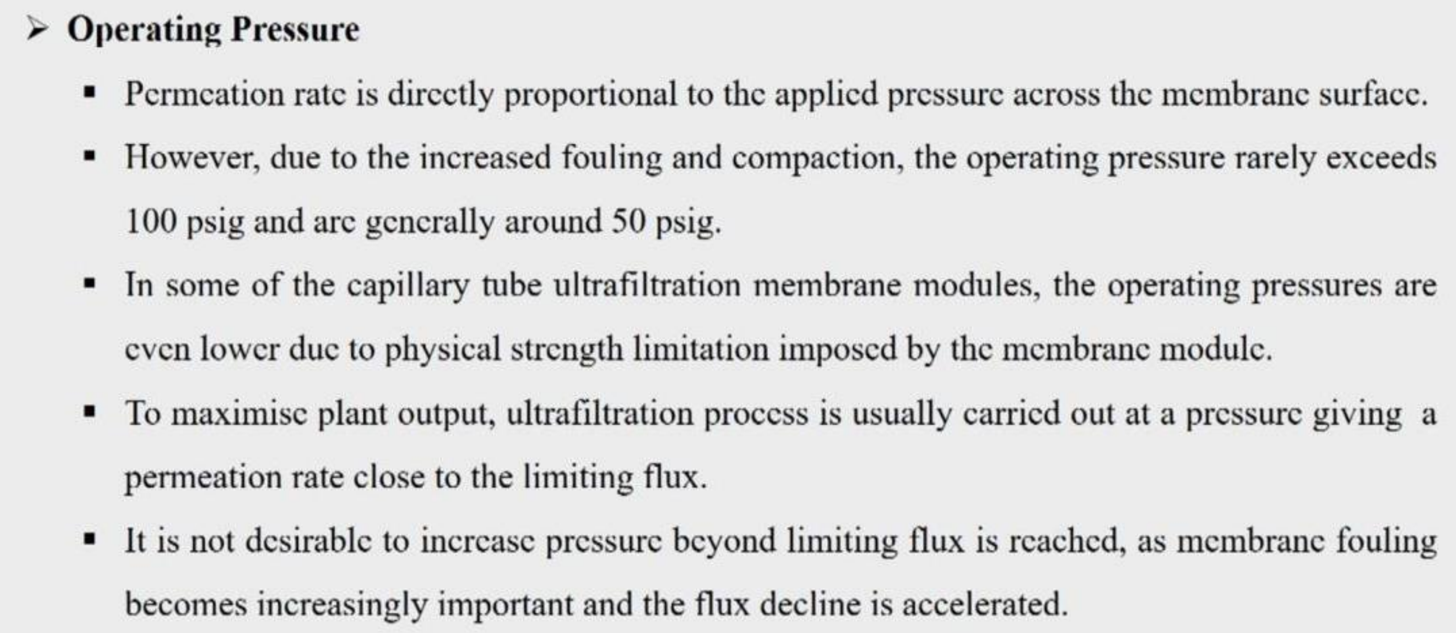


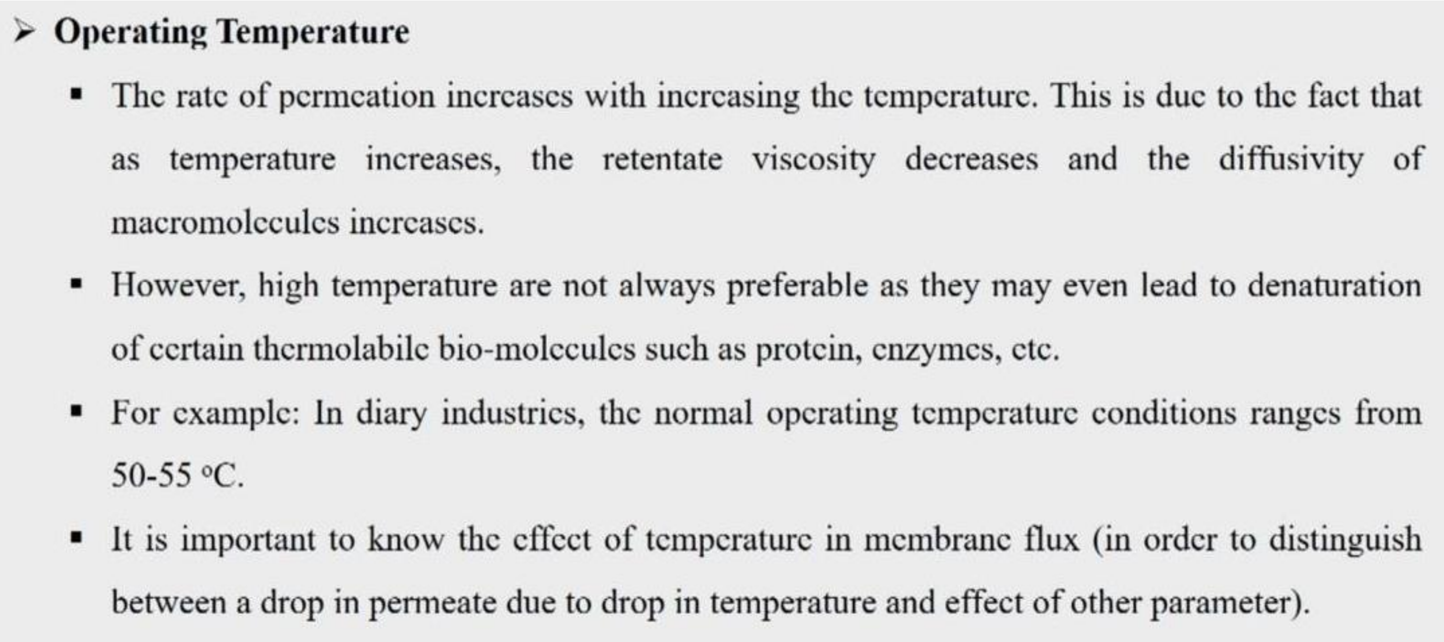
Ultrafiltration process

❑ Factors affecting UF performance

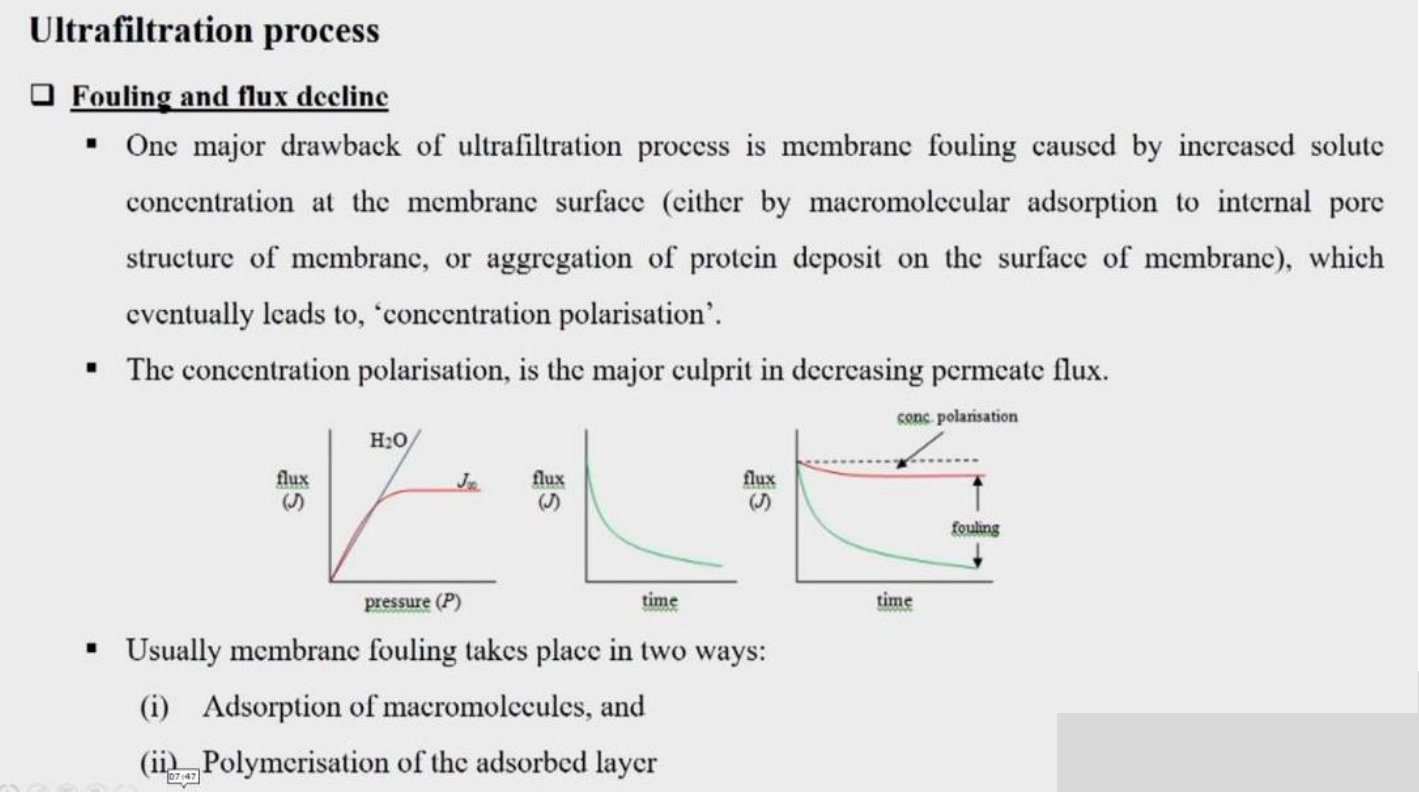
- **Transmembrane Flow**
  - The rate of permeation increases with increase in flow velocity of the liquid across the membrane surface.
  - Flow velocity is particularly important for liquids containing emulsions or suspensions.
  - Moreover, higher flow rate means higher energy consumption and larger pumps. Increasing the flow velocity also reduces the fouling on membrane surface.
  - Generally, an optimum flow velocity is arrived by a trade off between the pump horsepower and the increase in permeation rate.
  - For laminar flow, in thin channel modules, flow velocities of 1-2 m/s are used.
  - In tubular modules, turbulent flow may be generated with velocities up to 5 m/s.



- **Operating Pressure**
  - Permeation rate is directly proportional to the applied pressure across the membrane surface.
  - However, due to the increased fouling and compaction, the operating pressure rarely exceeds 100 psig and are generally around 50 psig.
  - In some of the capillary tube ultrafiltration membrane modules, the operating pressures are even lower due to physical strength limitation imposed by the membrane module.
  - To maximise plant output, ultrafiltration process is usually carried out at a pressure giving a permeation rate close to the limiting flux.
  - It is not desirable to increase pressure beyond limiting flux is reached, as membrane fouling becomes increasingly important and the flux decline is accelerated.



- **Operating Temperature**
  - The rate of permeation increases with increasing the temperature. This is due to the fact that as temperature increases, the retentate viscosity decreases and the diffusivity of macromolecules increases.
  - However, high temperature are not always preferable as they may even lead to denaturation of certain thermolabile bio-molecules such as protein, enzymes, etc.
  - For example: In diary industries, the normal operating temperature conditions ranges from 50-55 °C.
  - It is important to know the effect of temperature in membrane flux (in order to distinguish between a drop in permeate due to drop in temperature and effect of other parameter).



Ultrafiltration process

☐ **Fouling and flux decline**

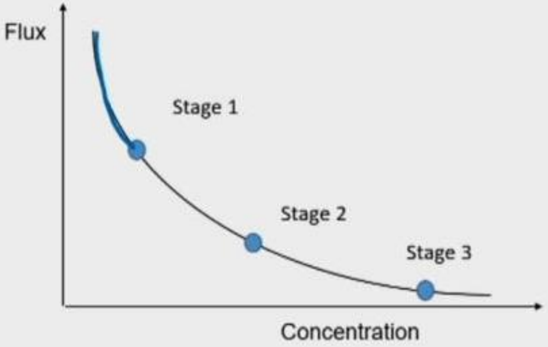
- One major drawback of ultrafiltration process is membrane fouling caused by increased solute concentration at the membrane surface (either by macromolecular adsorption to internal pore structure of membrane, or aggregation of protein deposit on the surface of membrane), which eventually leads to, 'concentration polarisation'.
- The concentration polarisation, is the major culprit in decreasing permeate flux.

- Usually membrane fouling takes place in two ways:
  - (i) Adsorption of macromolecules, and
  - (ii) Polymerisation of the adsorbed layer

☐ Fouling and flux decline

There are effectively three stages of flux decline:

- *Stage 1* is solvent (water) flux decline, in which UF membranes may lose about 50% of their permeability. Low concentration of contaminant particles, dust, or so are rapidly carried to and obstruct the largest pores.
- *Stage 2* is the initial polarisation period, in which the flux drops due to boundary layer phenomenon, and simultaneously, fouling is initiated by the plugging of pores with solutes.
- *Stage 3* is the period of normal UF operation during which polarised solute molecules may become bound to each other and to the membranes forming a deposits that no longer responds reversibly to the increases in cross-flow.

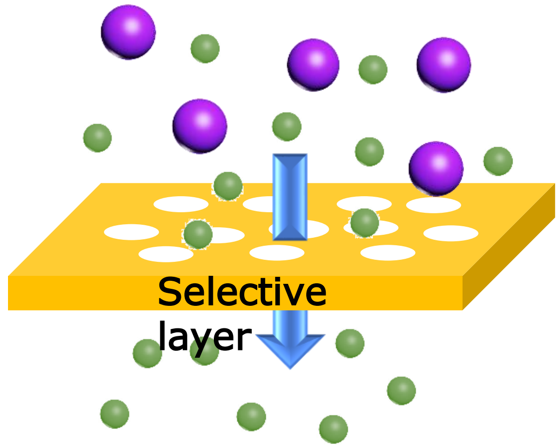


☐ Fouling and flux decline

- There are several methods to prevent fouling. These includes the pre-treatment of the feed water and the cleaning of the membranes.
- The pre-treatment method includes sand filtering, coagulation followed by an activated carbon adsorption, and dosing by oxidant agents or anti-fouling agents.
- The membranes are usually cleaned by chemicals or by back-flushing with pure water or permeate.
- pH adjustment can be used so that protein solutes will be far from their isoelectric point and so increase their solubility.
- Heat pre-treatment can be used to accelerate the precipitation tendency of fouling substances.
- Example: If cheese whey is kept for one hour at 65 °C, the immunoglobulins and the fat, the two least soluble components of whey are precipitated.

PROSES PEMISAHAN

Reverse Osmosis (RO)



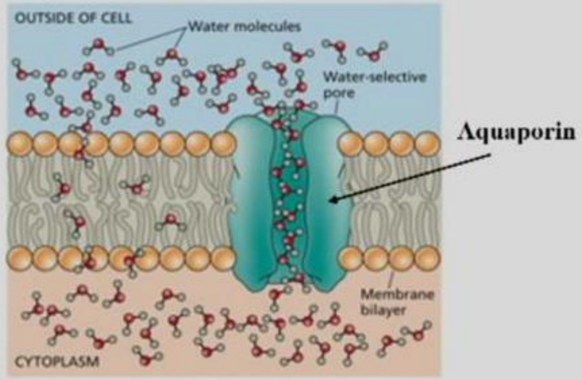
Oleh : Indah Prihatiningtyas D.S

Concept of Osmosis

- The word ‘osmosis’ is originated from the Greek work ‘*osmos*’ which means ‘to push’.
- Osmosis, is a natural phenomenon, most commonly observed in plants.
- A plant cell is a semi-permeable membrane (water flows through the membrane but salts do not) with the living stuff inside in a salt solution.
- Water is drawn into the cell from outside because pure water moves across a semi-permeable membrane to dilute the high concentration of salt inside.
- This is how water is drawn in from the ground when we water our plants.

Concept of Osmosis

- Diffusion of water across takes place by a selectively permeable membrane (a barrier that allows some substances to pass but not others).
- The cell membrane is such a barrier.
  - Small molecules pass through
    Example: water
  - Large molecules can’t pass through
    Example: Proteins and carbohydrates



Water channels (**aquaporins**) facilitate water transport across the plasma membrane – diffusion of water into or out of the cell from high to low water concentration.

Concept of Osmosis

- An osmotic pressure arises when two solutions of different concentration (or a pure solvent and a solution) are separated by a semi-permeable membrane i.e. one which is permeable to solvent but impermeable to solute.
- Here, the membrane separates two liquid phases: a **concentrated phase 1**, and a **dilute phase 2**.

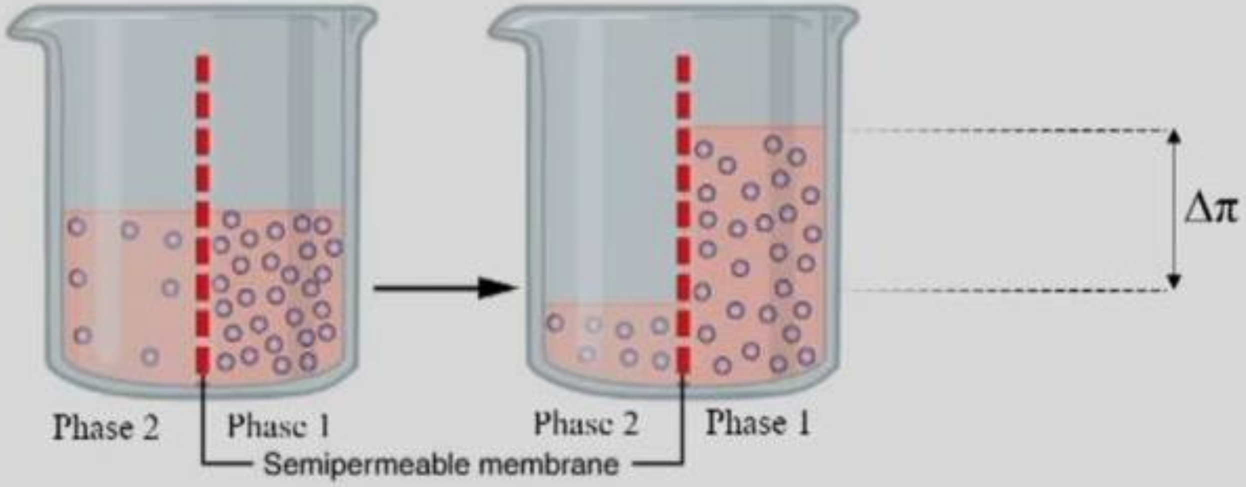
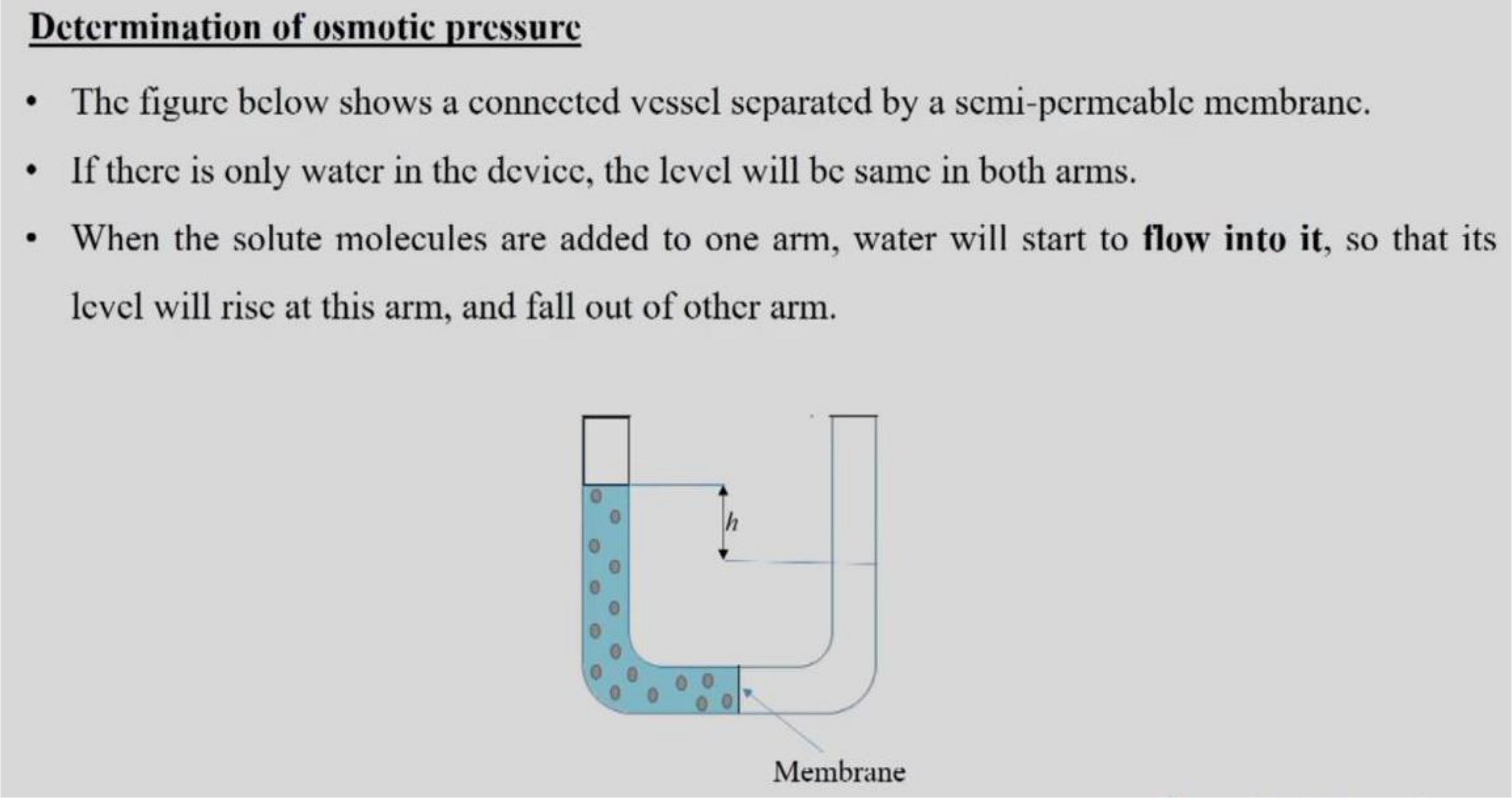
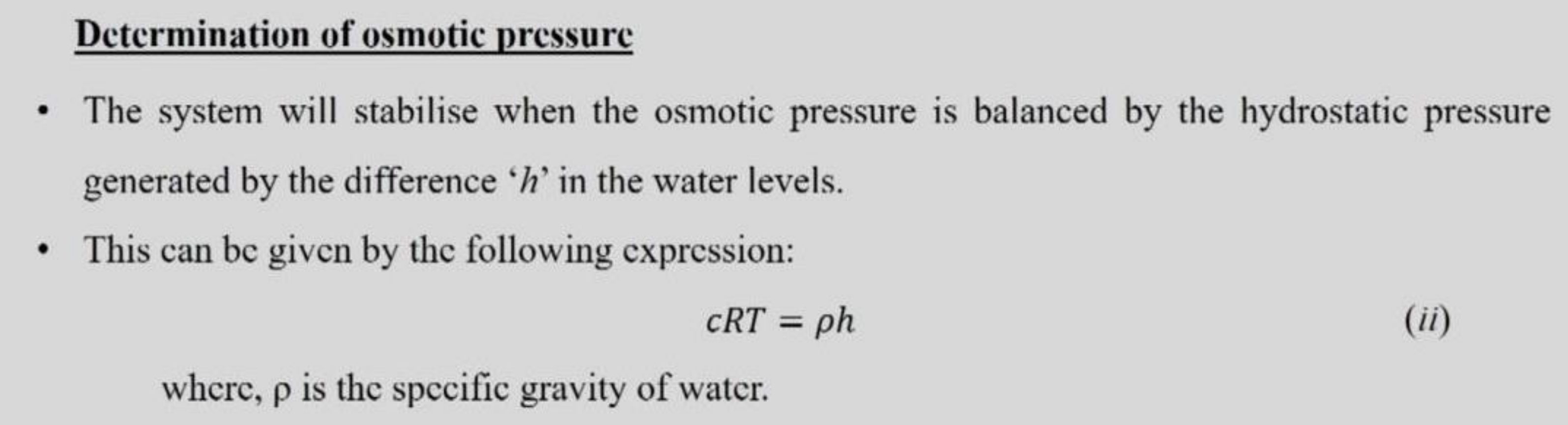


Figure. Schematic representation of osmosis



Determination of osmotic pressure

- The figure below shows a connected vessel separated by a semi-permeable membrane.
- If there is only water in the device, the level will be same in both arms.
- When the solute molecules are added to one arm, water will start to **flow into it**, so that its level will rise at this arm, and fall out of other arm.



Determination of osmotic pressure

- The system will stabilise when the osmotic pressure is balanced by the hydrostatic pressure generated by the difference '*h*' in the water levels.
- This can be given by the following expression:

$$cRT = \rho h \qquad (ii)$$

where, ρ is the specific gravity of water.

Osmotic pressure is closely related to the colligative properties of a solution such as freezing point depression and boiling point elevation [27]. For ideal dilute solutions, the osmotic pressure (π) can be estimated using the van't Hoff equation given below [28]:

$$\pi = CRT \tag{1}$$

where, C is the molar concentration of a non-permeable solute in the solution (mol/L), R is the universal gas constant (0.08206 L atm/mol K), and T is the absolute temperature (K).

In case of non-ideal dilute solutions, the osmotic pressure is given by the power series shown below [29]:

$$\pi = RT\left(\frac{\rho_2}{M_2} + A_2\rho_2^2 + A_3\rho_2^3 + \ldots\right) \tag{2}$$

where, M_2 is molar mass of the solute, A_2, A_3, and so on are the second, third, etc. virial coefficients, and ρ_2 is the solute mass concentration (g/L).

For non-ideal concentrated solutions, the following logarithmic equation is valid for the estimation of osmotic pressure [29]:

$$\pi = -\frac{RT}{V_1^0}\ln(a_1) \tag{3}$$

where, a_1 is the activity of the solvent and $V_1{}^0$ is the molar volume of pure solvent (L/mol).

When several electrolytes are present in the solution, the osmotic pressure can be calculated as follows [30]:

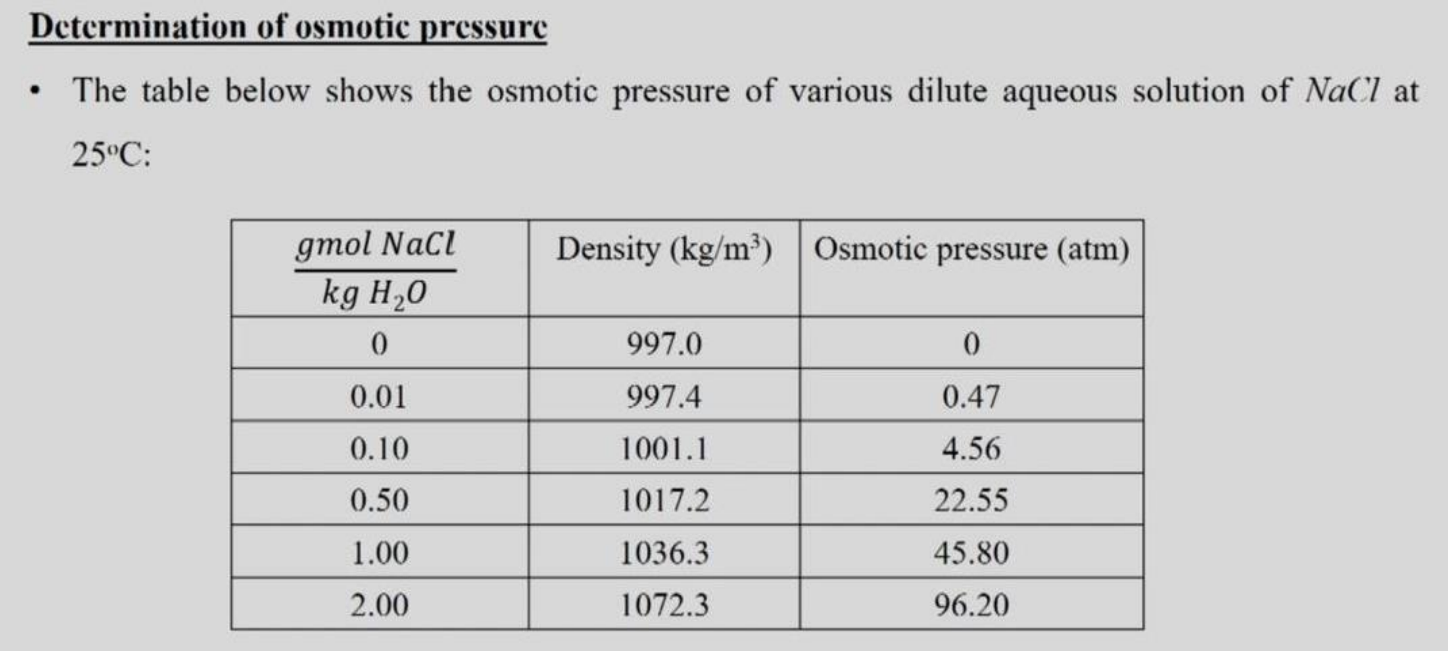
$$\pi = \varphi RT \sum \nu_i C_i \tag{4}$$

where, ν_i and C_i represent the number of ions and molar concentration of the electrolyte i and φ is the osmotic coefficient that can be determined by conducting experiments (such as freezing point depression measurements or vapor pressure osmometry) or using Pitzer correlation [31]. In case of RO using seawater feed, the following approximate expression for osmotic pressure can be employed [23,26,32]:

$$\pi = 1.12T \sum m_i \tag{5}$$

where, π is in psia, T is in K, and the term Σm_i represents the summation of molarities (mol/L) of all the dissolved species (both ionic and non-ionic) in the solution.

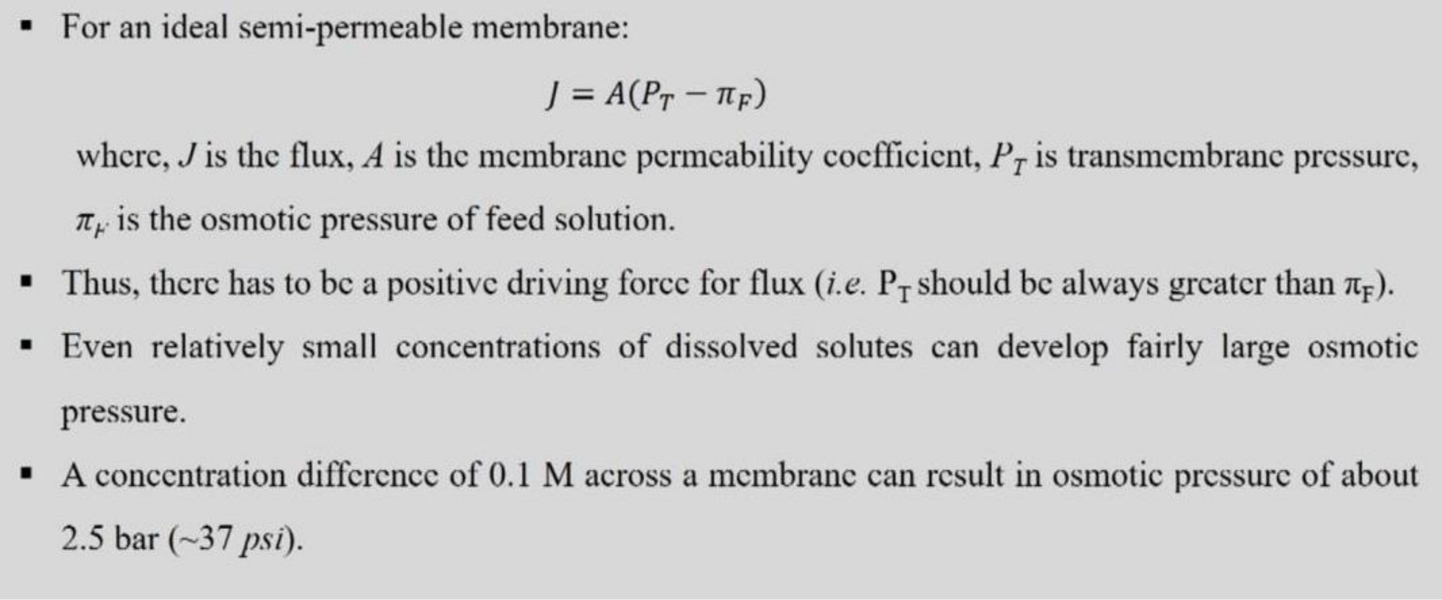
As a rule of thumb, osmotic pressure ranges from 0.60 to 1.1 psi for every 100 ppm of total dissolved solids (TDS) in the solution [33]. For instance, the osmotic pressure of seawater with TDS content of 35,000 ppm would be around 350 psi. However, it should be noted that due to the high resistance of the membrane, the pressure applied in RO must be significantly higher than the osmotic pressure. For example, in case of RO using seawater with TDS content of 35,000 ppm, pressures as high as 1500 psi may be required [33].



Determination of osmotic pressure

- The table below shows the osmotic pressure of various dilute aqueous solution of *NaCl* at 25°C:

$\frac{gmol\ NaCl}{kg\ H_2O}$	Density (kg/m^3)	Osmotic pressure (atm)
0	997.0	0
0.01	997.4	0.47
0.10	1001.1	4.56
0.50	1017.2	22.55
1.00	1036.3	45.80
2.00	1072.3	96.20

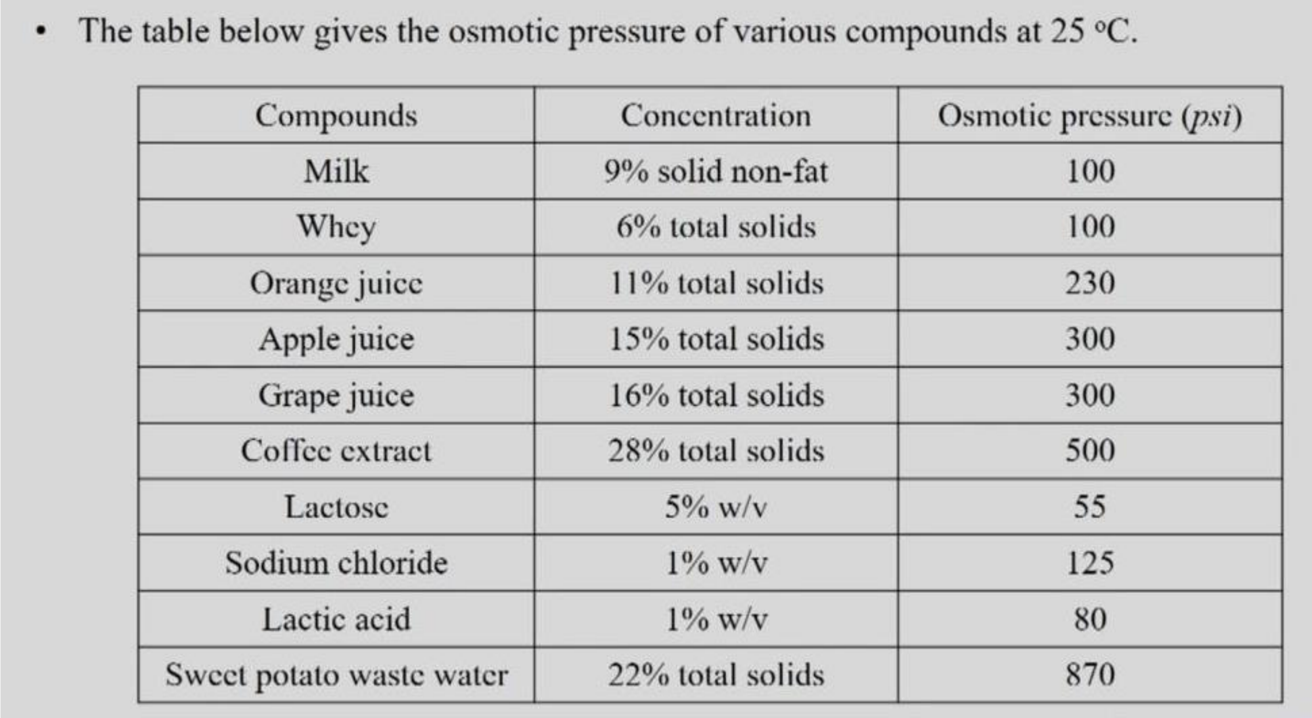


- For an ideal semi-permeable membrane:

$$J = A(P_T - \pi_F)$$

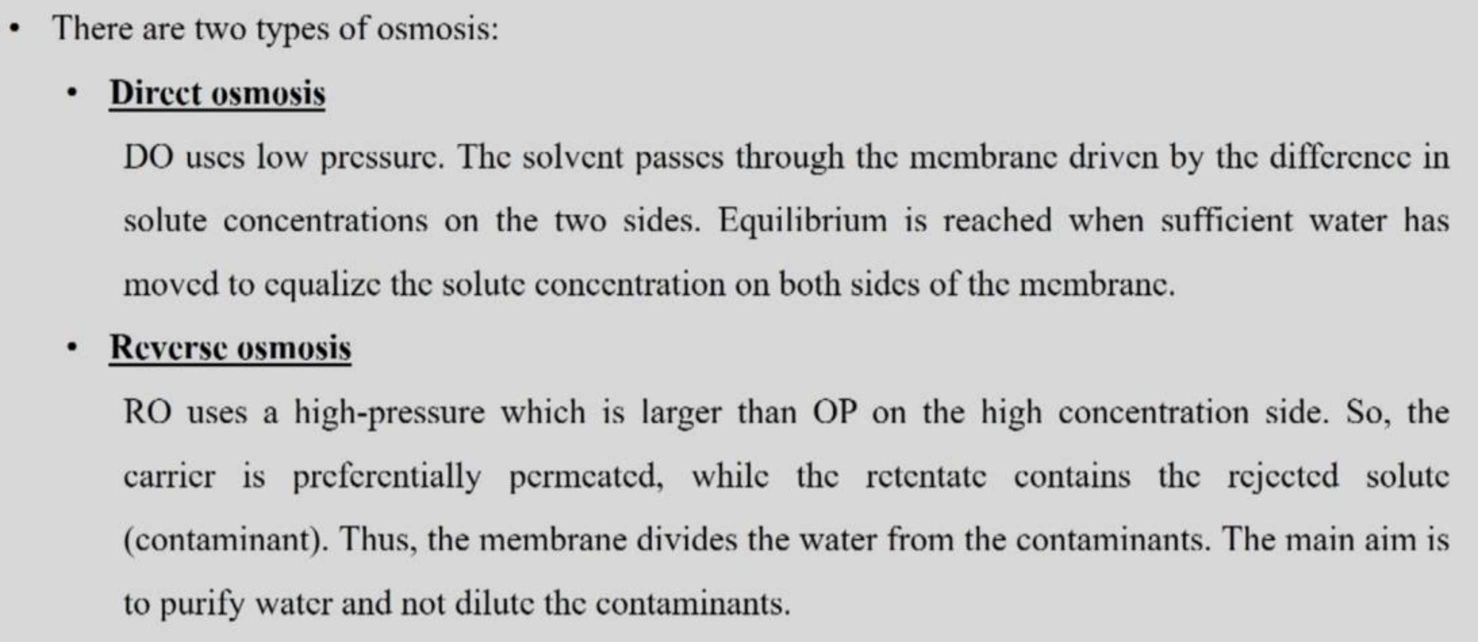
where, J is the flux, A is the membrane permeability coefficient, P_T is transmembrane pressure, π_F is the osmotic pressure of feed solution.

- Thus, there has to be a positive driving force for flux (*i.e.* P_T should be always greater than π_F).
- Even relatively small concentrations of dissolved solutes can develop fairly large osmotic pressure.
- A concentration difference of 0.1 M across a membrane can result in osmotic pressure of about 2.5 bar (~37 *psi*).



- The table below gives the osmotic pressure of various compounds at 25 °C.

Compounds	Concentration	Osmotic pressure (*psi*)
Milk	9% solid non-fat	100
Whey	6% total solids	100
Orange juice	11% total solids	230
Apple juice	15% total solids	300
Grape juice	16% total solids	300
Coffee extract	28% total solids	500
Lactose	5% w/v	55
Sodium chloride	1% w/v	125
Lactic acid	1% w/v	80
Sweet potato waste water	22% total solids	870

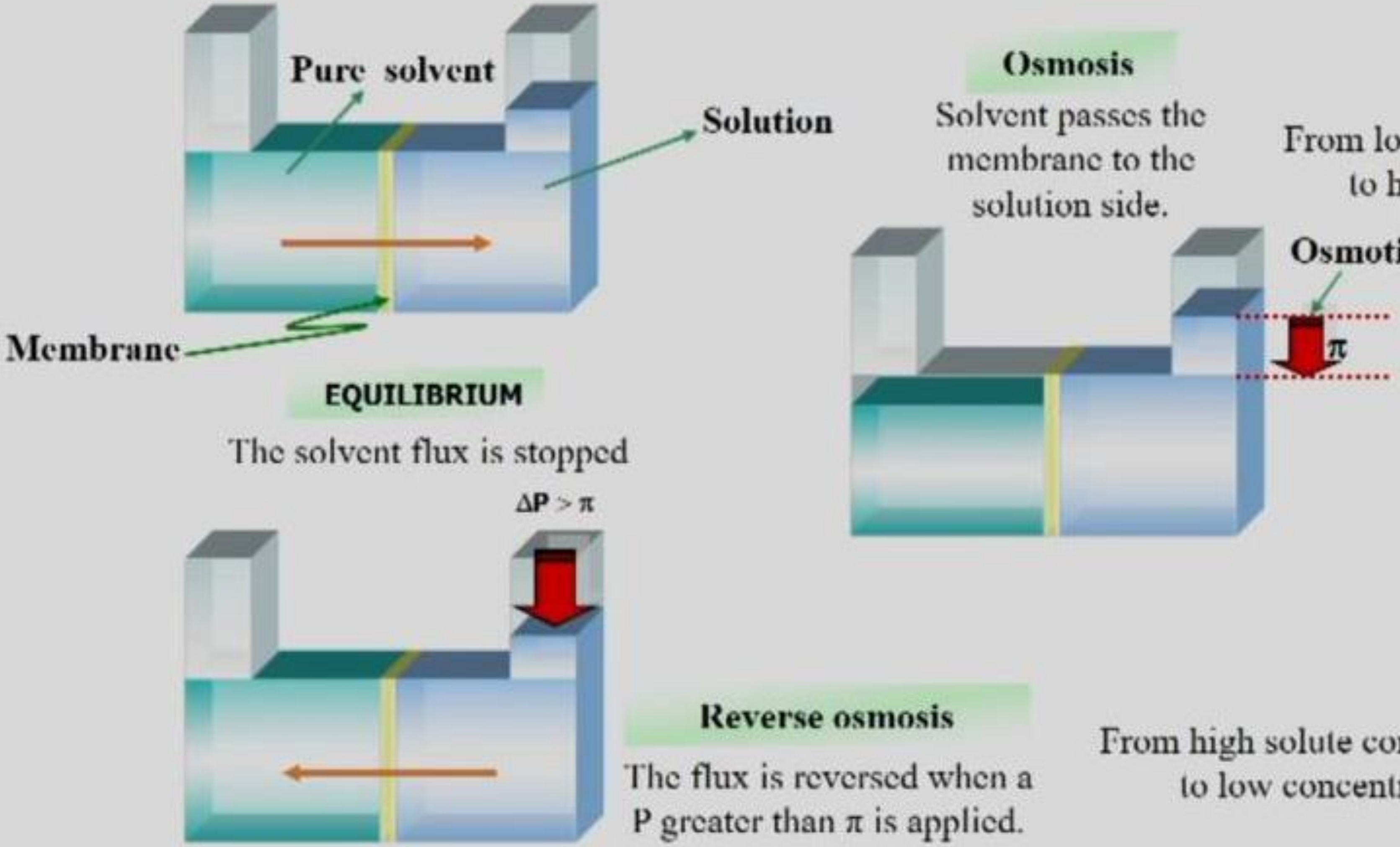


- There are two types of osmosis:
  - **Direct osmosis**

    DO uses low pressure. The solvent passes through the membrane driven by the difference in solute concentrations on the two sides. Equilibrium is reached when sufficient water has moved to equalize the solute concentration on both sides of the membrane.
  - **Reverse osmosis**

    RO uses a high-pressure which is larger than OP on the high concentration side. So, the carrier is preferentially permeated, while the retentate contains the rejected solute (contaminant). Thus, the membrane divides the water from the contaminants. The main aim is to purify water and not dilute the contaminants.

Concept of Osmosis & Reverse Osmosis



EQUILIBRIUM

The solvent flux is stopped

Osmosis

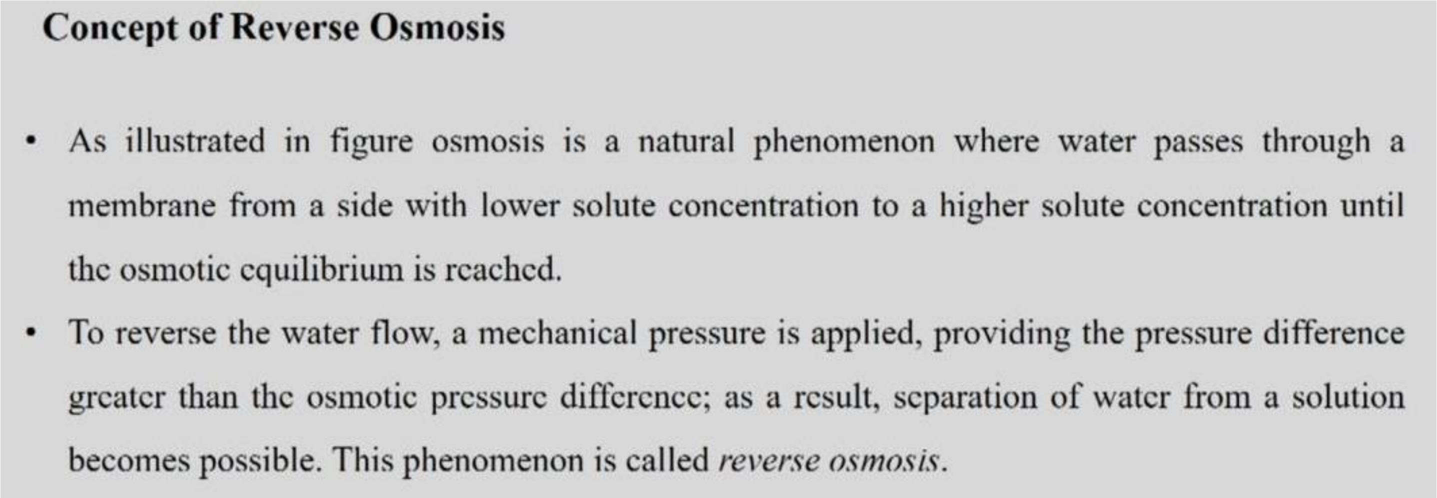
Solvent passes the membrane to the solution side.

From low solute concentration to high concentration.

Reverse osmosis

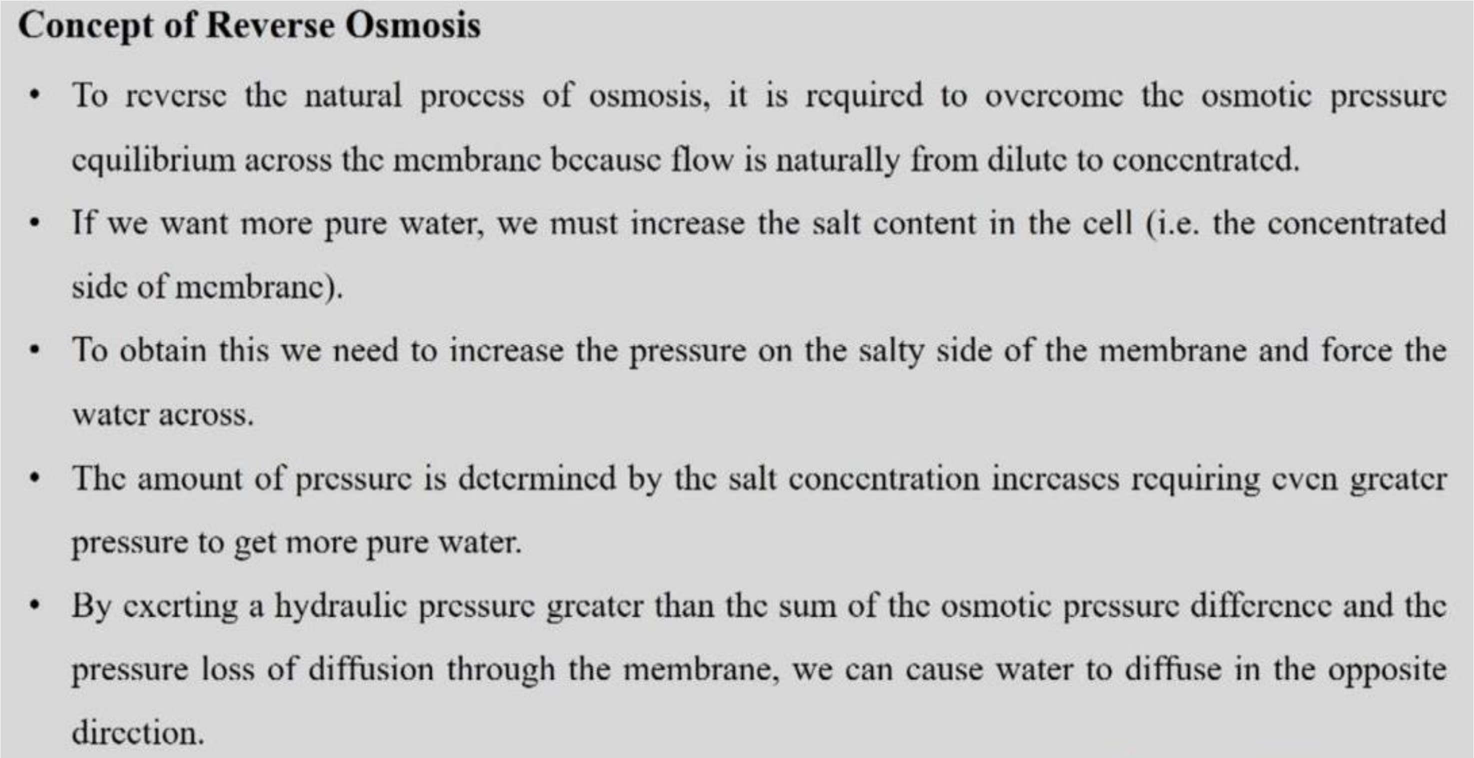
The flux is reversed when a P greater than π is applied.

From high solute concentration to low concentration



Concept of Reverse Osmosis

- As illustrated in figure osmosis is a natural phenomenon where water passes through a membrane from a side with lower solute concentration to a higher solute concentration until the osmotic equilibrium is reached.
- To reverse the water flow, a mechanical pressure is applied, providing the pressure difference greater than the osmotic pressure difference; as a result, separation of water from a solution becomes possible. This phenomenon is called *reverse osmosis*.



Concept of Reverse Osmosis

- To reverse the natural process of osmosis, it is required to overcome the osmotic pressure equilibrium across the membrane because flow is naturally from dilute to concentrated.
- If we want more pure water, we must increase the salt content in the cell (i.e. the concentrated side of membrane).
- To obtain this we need to increase the pressure on the salty side of the membrane and force the water across.
- The amount of pressure is determined by the salt concentration increases requiring even greater pressure to get more pure water.
- By exerting a hydraulic pressure greater than the sum of the osmotic pressure difference and the pressure loss of diffusion through the membrane, we can cause water to diffuse in the opposite direction.

Concept of Reverse Osmosis

- The greater the pressure applied, the more rapid will be diffusion. It follows that if other variables are kept constant, the water flow-rate becomes proportional to the net pressure.
- Using reverse osmosis, it is possible to concentrate various solutes, either dissolved or dispersed, in a solution.
- It has the separation range of 0.0001 - 0.001 µm particle size.

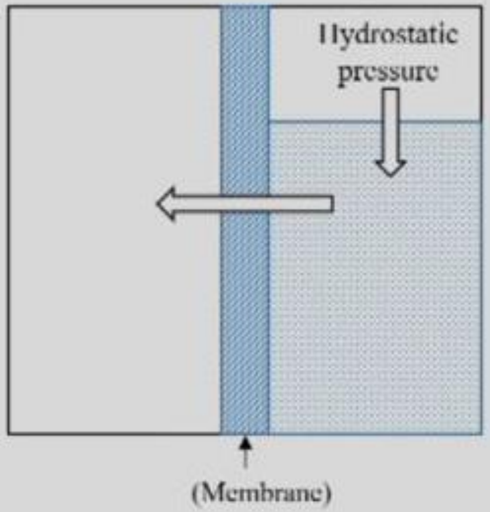
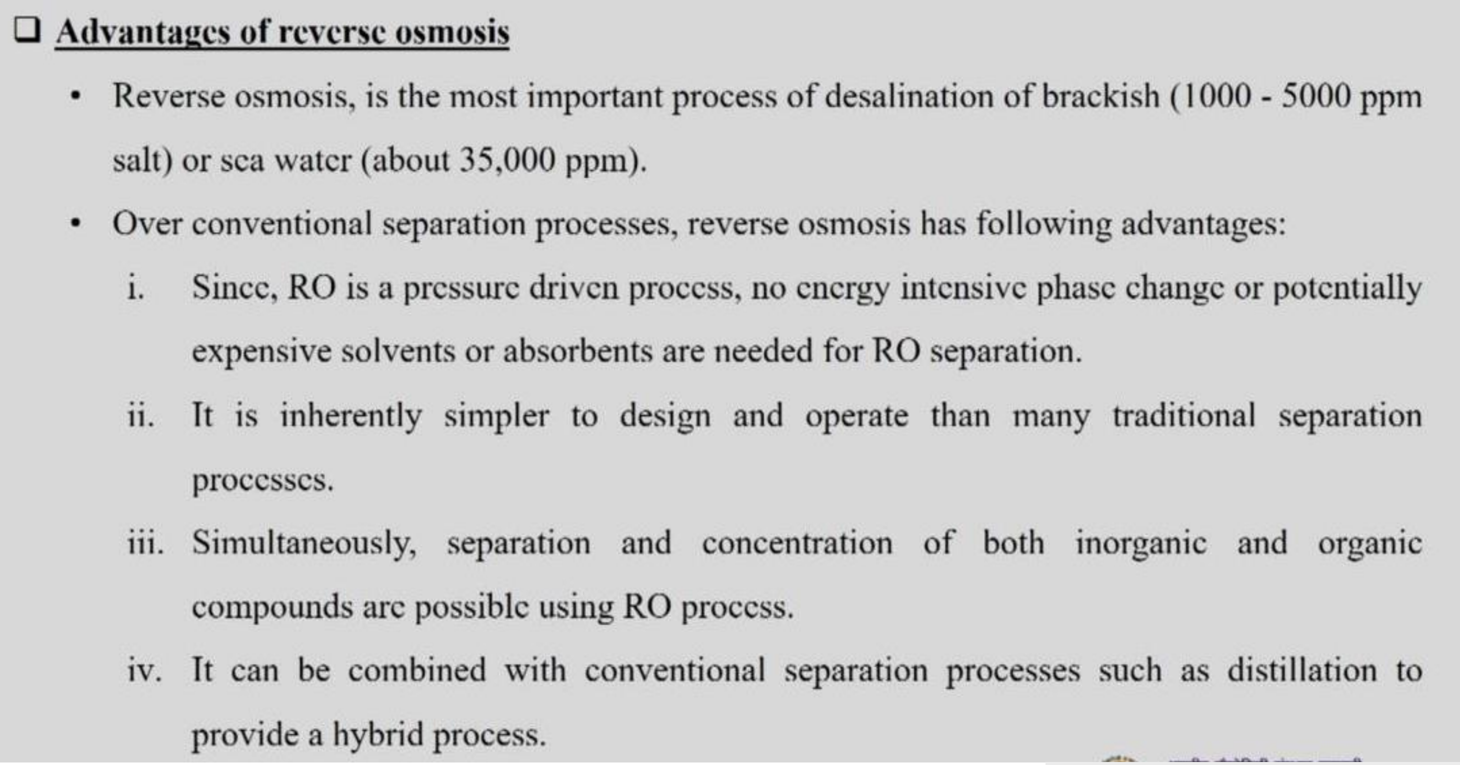
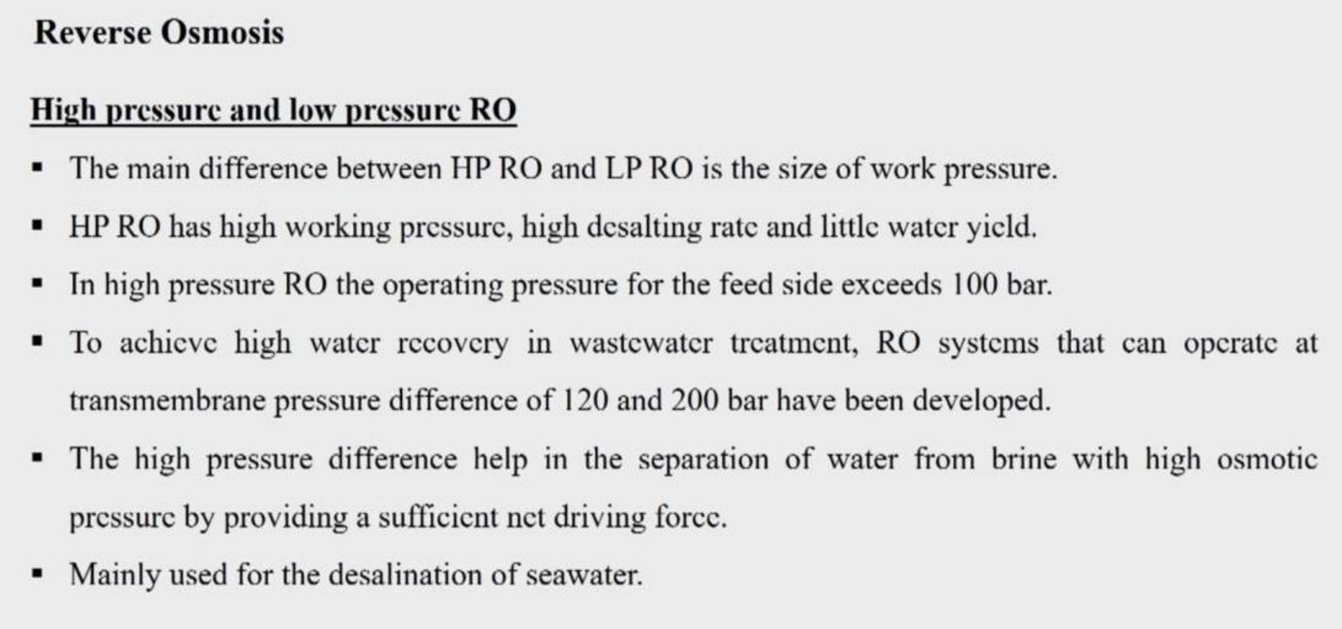


Figure. Hydrostatic pressure causing reverse osmosis



❑ Advantages of reverse osmosis

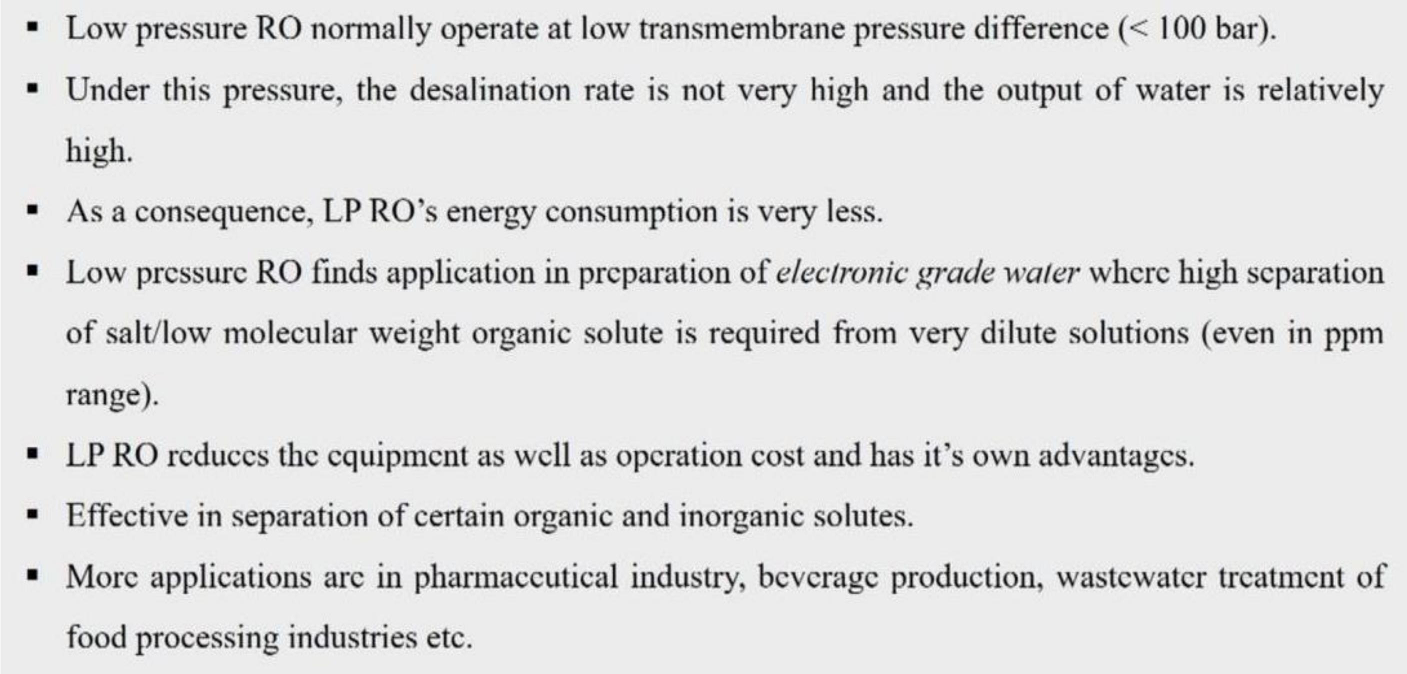
- Reverse osmosis, is the most important process of desalination of brackish (1000 - 5000 ppm salt) or sea water (about 35,000 ppm).
- Over conventional separation processes, reverse osmosis has following advantages:
  - i. Since, RO is a pressure driven process, no energy intensive phase change or potentially expensive solvents or absorbents are needed for RO separation.
  - ii. It is inherently simpler to design and operate than many traditional separation processes.
  - iii. Simultaneously, separation and concentration of both inorganic and organic compounds are possible using RO process.
  - iv. It can be combined with conventional separation processes such as distillation to provide a hybrid process.



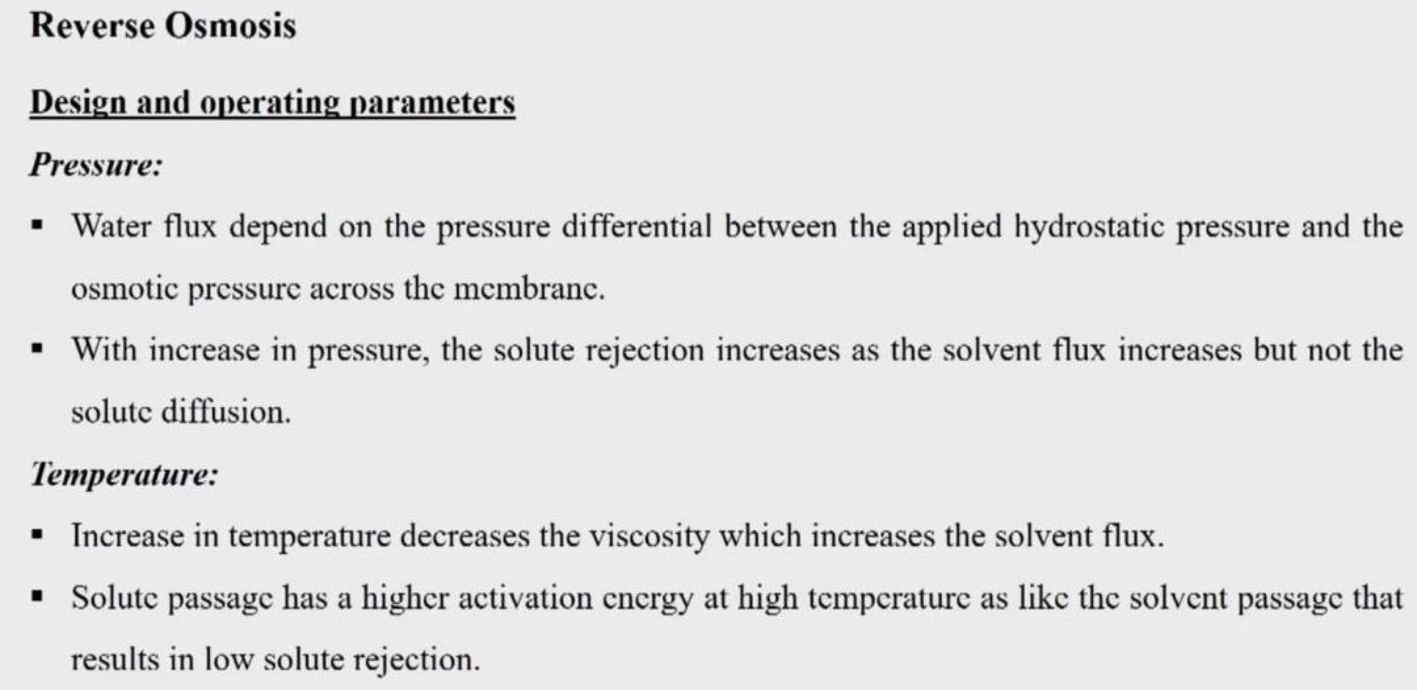
Reverse Osmosis

High pressure and low pressure RO

- The main difference between HP RO and LP RO is the size of work pressure.
- HP RO has high working pressure, high desalting rate and little water yield.
- In high pressure RO the operating pressure for the feed side exceeds 100 bar.
- To achieve high water recovery in wastewater treatment, RO systems that can operate at transmembrane pressure difference of 120 and 200 bar have been developed.
- The high pressure difference help in the separation of water from brine with high osmotic pressure by providing a sufficient net driving force.
- Mainly used for the desalination of seawater.



- Low pressure RO normally operate at low transmembrane pressure difference (< 100 bar).
- Under this pressure, the desalination rate is not very high and the output of water is relatively high.
- As a consequence, LP RO's energy consumption is very less.
- Low pressure RO finds application in preparation of *electronic grade water* where high separation of salt/low molecular weight organic solute is required from very dilute solutions (even in ppm range).
- LP RO reduces the equipment as well as operation cost and has it's own advantages.
- Effective in separation of certain organic and inorganic solutes.
- More applications are in pharmaceutical industry, beverage production, wastewater treatment of food processing industries etc.



Reverse Osmosis

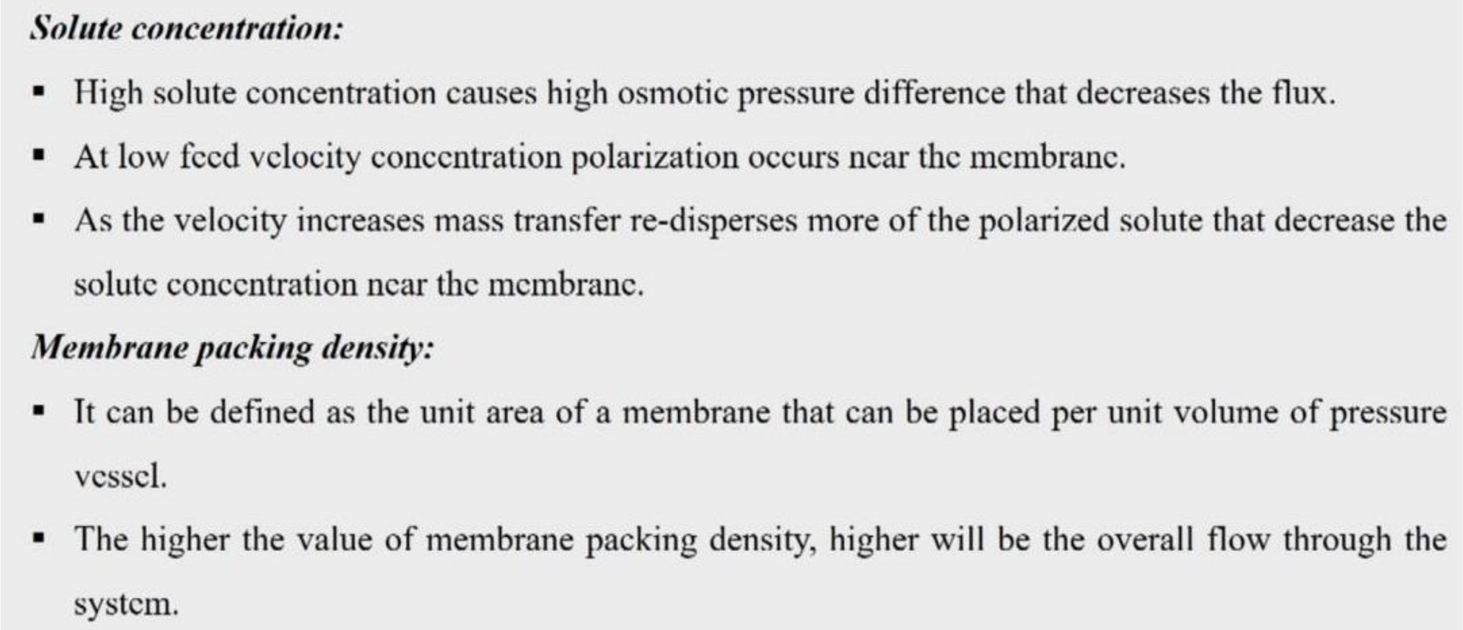
Design and operating parameters

Pressure:

- Water flux depend on the pressure differential between the applied hydrostatic pressure and the osmotic pressure across the membrane.
- With increase in pressure, the solute rejection increases as the solvent flux increases but not the solute diffusion.

Temperature:

- Increase in temperature decreases the viscosity which increases the solvent flux.
- Solute passage has a higher activation energy at high temperature as like the solvent passage that results in low solute rejection.

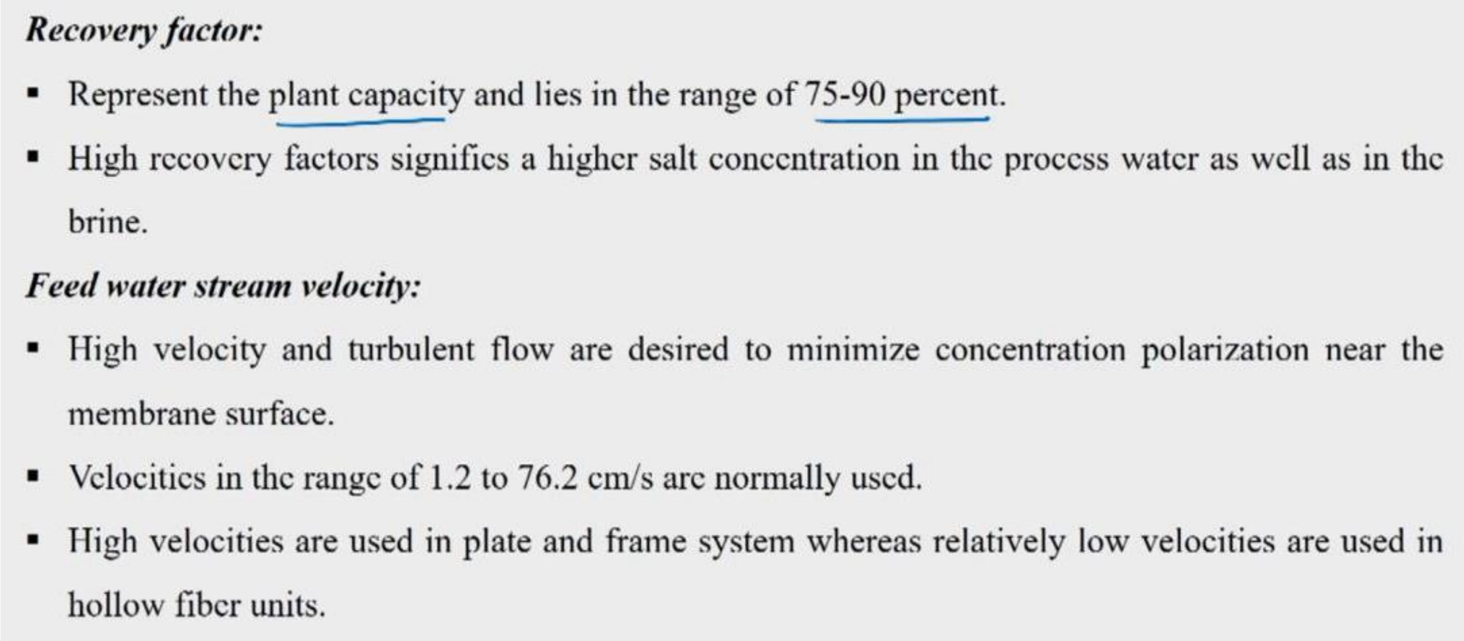


Solute concentration:

- High solute concentration causes high osmotic pressure difference that decreases the flux.
- At low feed velocity concentration polarization occurs near the membrane.
- As the velocity increases mass transfer re-disperses more of the polarized solute that decrease the solute concentration near the membrane.

Membrane packing density:

- It can be defined as the unit area of a membrane that can be placed per unit volume of pressure vessel.
- The higher the value of membrane packing density, higher will be the overall flow through the system.

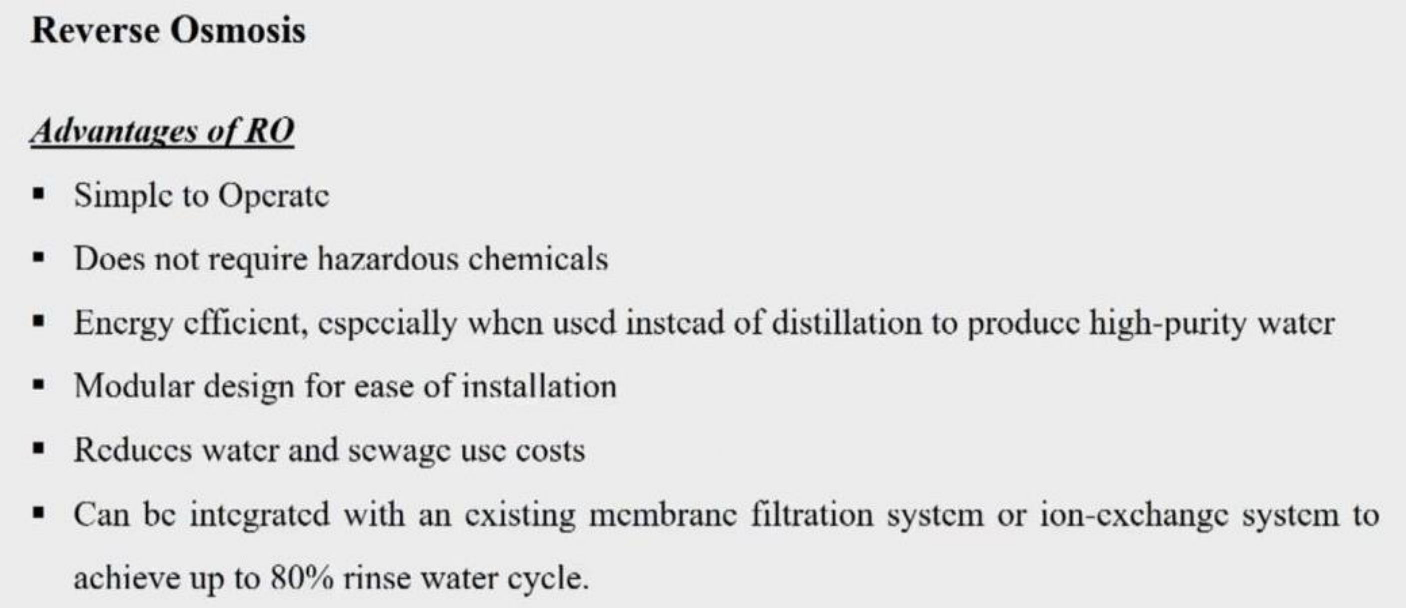


Recovery factor:

- Represent the plant capacity and lies in the range of 75-90 percent.
- High recovery factors signifies a higher salt concentration in the process water as well as in the brine.

Feed water stream velocity:

- High velocity and turbulent flow are desired to minimize concentration polarization near the membrane surface.
- Velocities in the range of 1.2 to 76.2 cm/s are normally used.
- High velocities are used in plate and frame system whereas relatively low velocities are used in hollow fiber units.



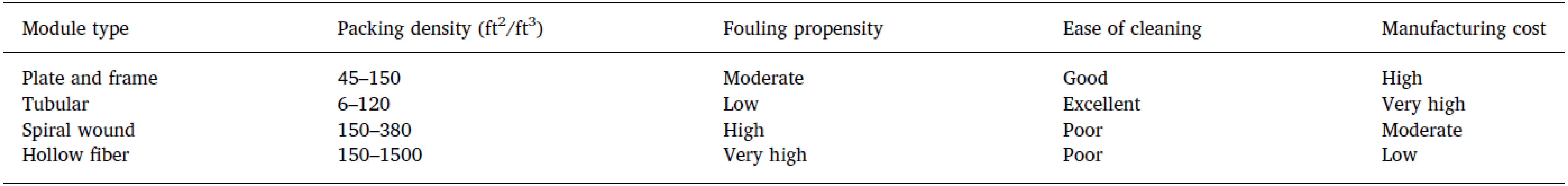
Reverse Osmosis

Advantages of RO

- Simple to Operate
- Does not require hazardous chemicals
- Energy efficient, especially when used instead of distillation to produce high-purity water
- Modular design for ease of installation
- Reduces water and sewage use costs
- Can be integrated with an existing membrane filtration system or ion-exchange system to achieve up to 80% rinse water cycle.

Membrane modules

Comparison of RO membrane modules [33,102].



Module type	Packing density (ft^2/ft^3)	Fouling propensity	Ease of cleaning	Manufacturing cost
Plate and frame	45–150	Moderate	Good	High
Tubular	6–120	Low	Excellent	Very high
Spiral wound	150–380	High	Poor	Moderate
Hollow fiber	150–1500	Very high	Poor	Low

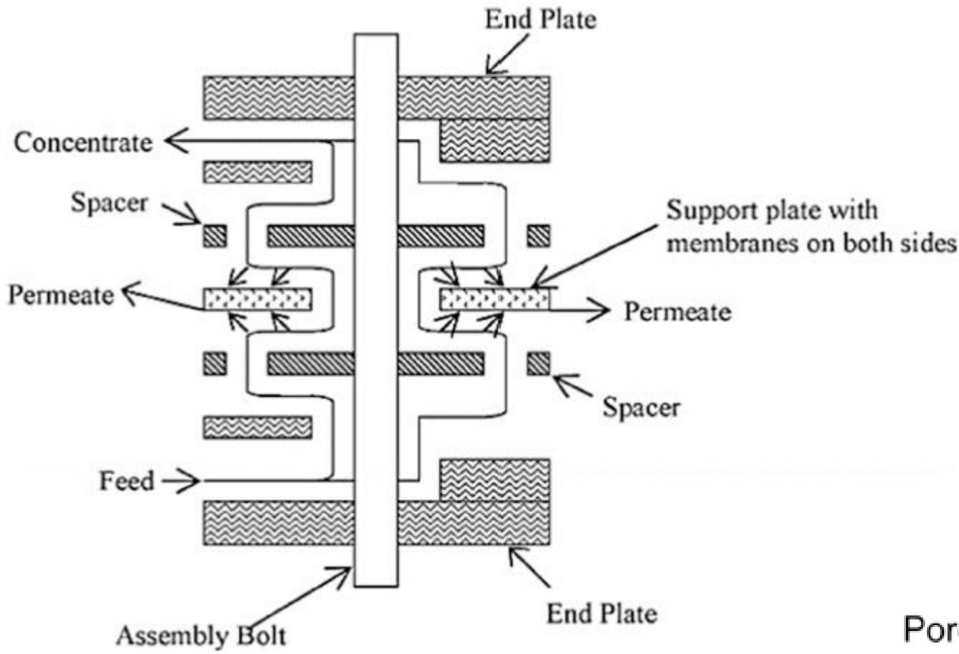


Fig. 4. Plate and frame membrane module. (Adopted from [104])

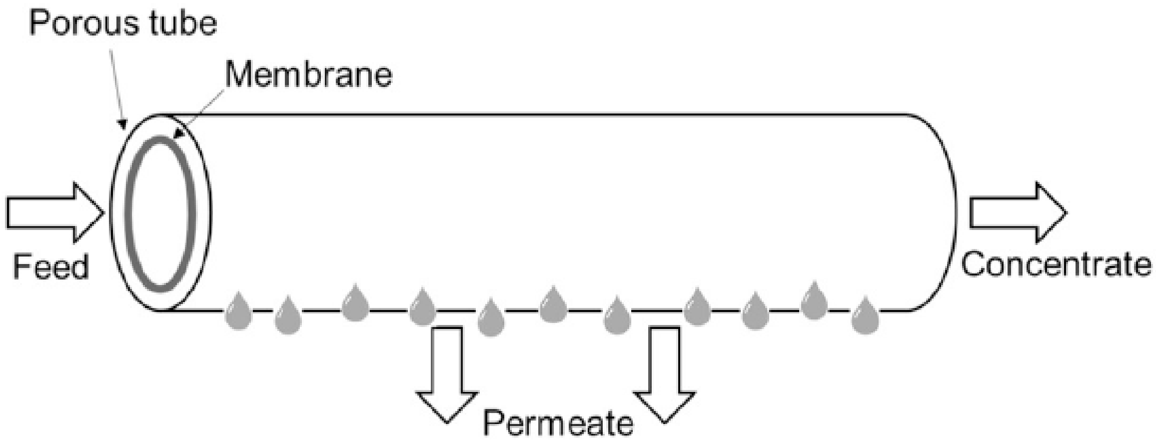


Fig. 5. Tubular RO membrane module. (Modified after [101])

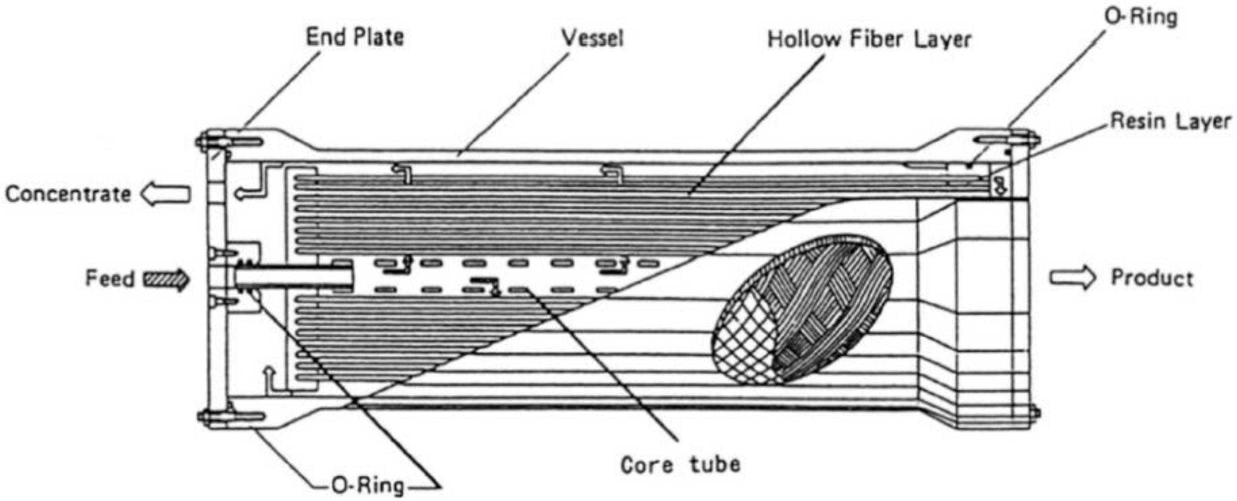


Fig. 6. Hollow fiber RO membrane module
(Adopted from [108])

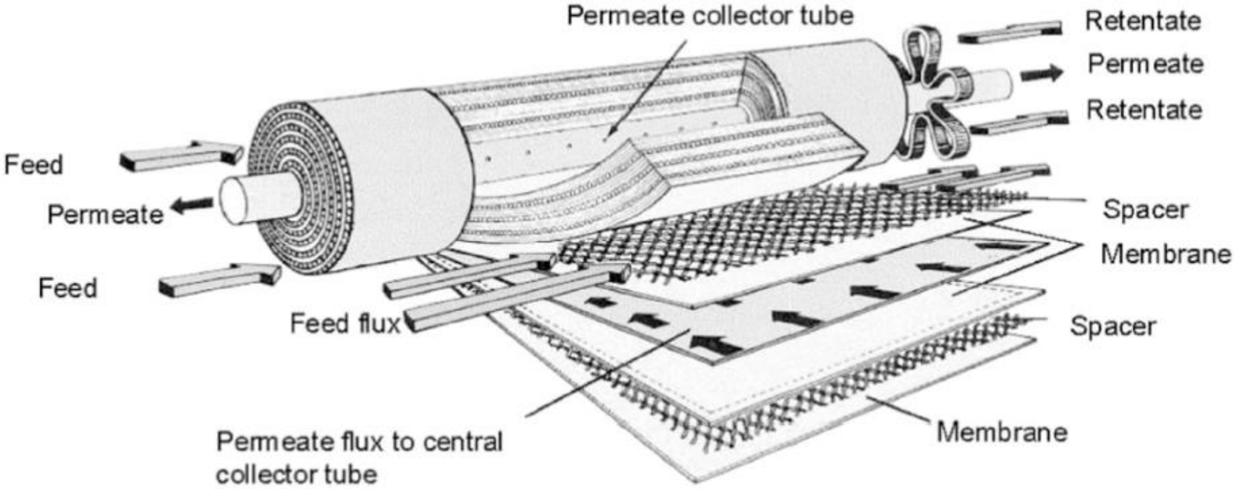
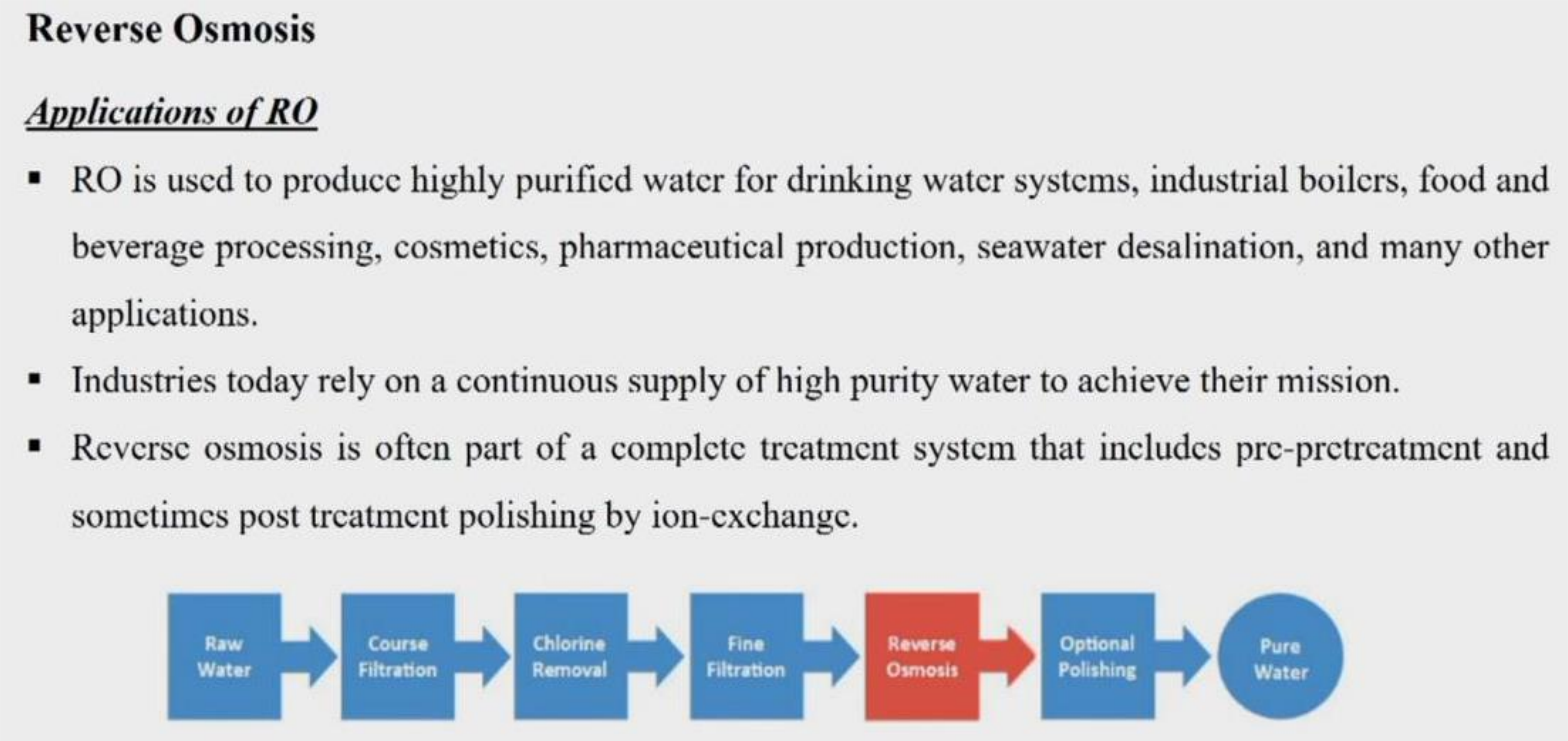


Fig. 7. Spiral wound RO membrane module.
(Adopted from [36])



Reverse Osmosis

Applications of RO

- RO is used to produce highly purified water for drinking water systems, industrial boilers, food and beverage processing, cosmetics, pharmaceutical production, seawater desalination, and many other applications.
- Industries today rely on a continuous supply of high purity water to achieve their mission.
- Reverse osmosis is often part of a complete treatment system that includes pre-pretreatment and sometimes post treatment polishing by ion-exchange.

Applications of RO: Seawater Desalination System

- Reverse osmosis membrane seawater desalination system removes salts from seawater to supply fresh water for drinking and industrial use.
- Ensures supplies of drinking water and domestic water on off-shore islands.
- Desalinization of water with a high salt concentration and well water near the seashore is possible.

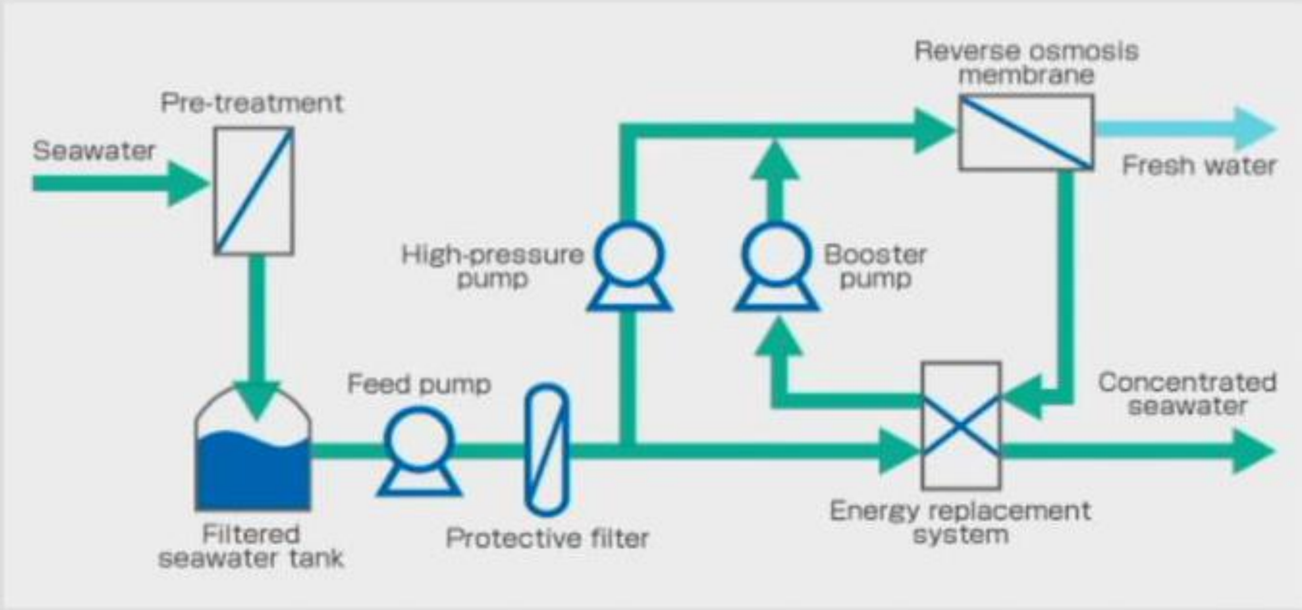


Fig: Reverse Osmosis Membrane Seawater Desalination System

Courtesy: Toyobo

Applications of RO: Seawater Concentration System

- Used to produce salt from deep ocean water and seawater.
- This can help to reduce the load on salt making machinery, lower energy costs, and improve production efficiency

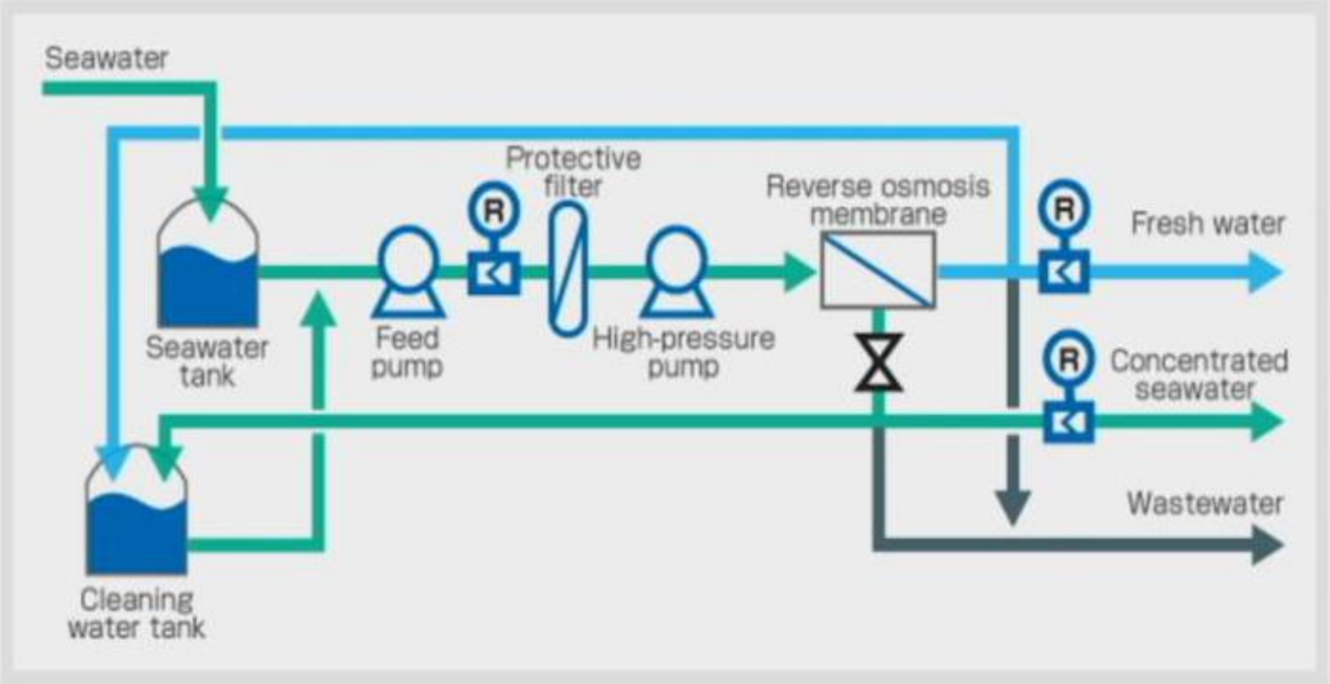


Fig. Reverse Osmosis Membrane Seawater Concentration System

Applications of RO: Reverse osmosis system in a boiler feed water system

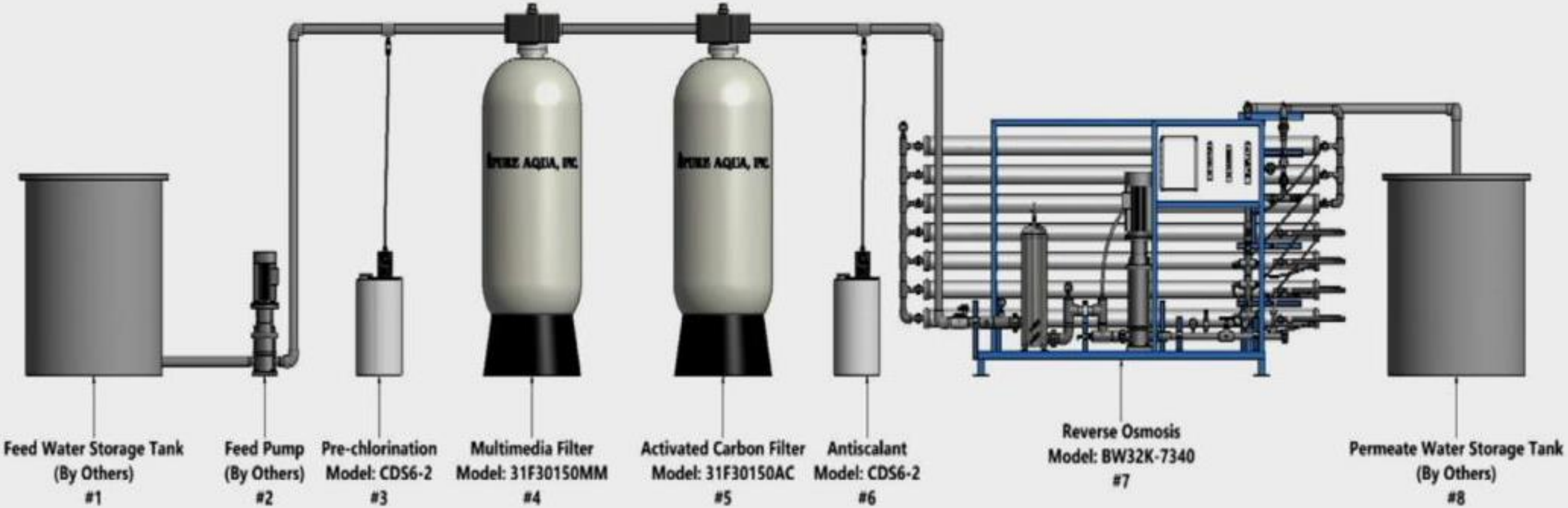


Fig. Reverse osmosis system in a boiler feed water system

Applications of RO: Reverse osmosis system in a boiler feed water system

- Reverse osmosis systems reduce the dissolved solids that lead to scaling.
- Removing these contaminates improves the boilers efficiency and increases its ability to work at full capacity.
- The right RO system design will utilize ASME pressure vessels, filter tanks and high-quality instruments such as conductivity, pH and ORP meters.
- Having a reverse osmosis system as boiler feed water pretreatment can:
    - ➢ Reduce fuel costs through lower heat loss and increased boiler cycles.
    - ➢ Reducing the total dissolved solids (TDS) in the RO product water can increase the boiler's cycles of concentration.
    - ➢ Improve operation and steam purity (because of availability of better quality feedwater to the boiler).
    - ➢ The amount of boiler feed chemicals required to prevent condensation corrosion is less due to lower alkalinity in the boiler makeup water.

Applications of RO: Beer Dealcoholisation process

- Pressurized beer (20–80 bar) is put in contact with a semi-permeable membrane to promote the permeation of alcohol and some water to the permeate side
- Larger molecules, such as aroma and flavor compounds, virtually remain on the concentrated side
- The amount of water lost is typically recovered and added to the feed or at the end of process for adjustment of the ethanol content in the product.

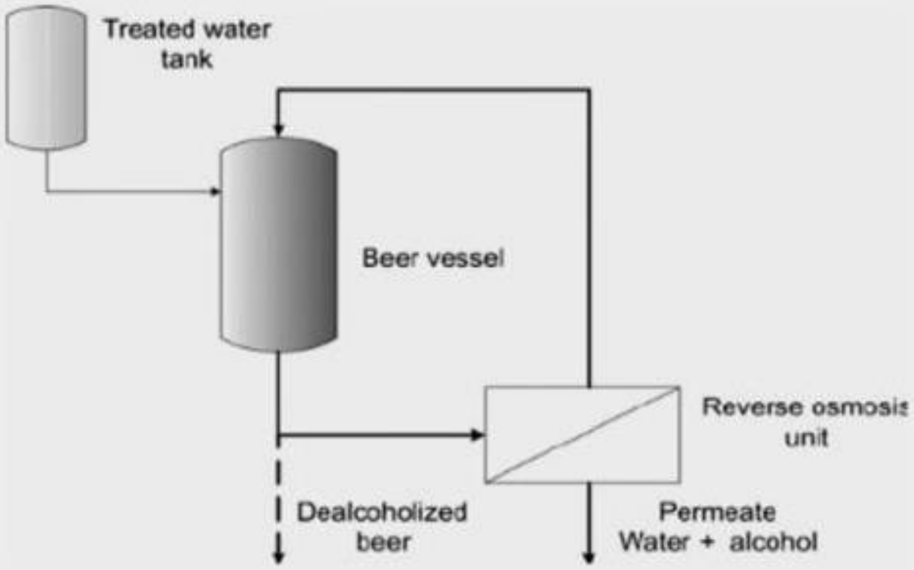


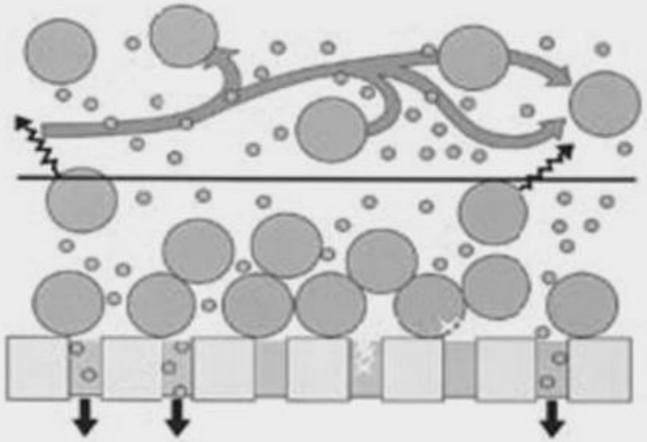
Fig. Typical flow chart of a beer dealcoholisation process by reverse osmosis

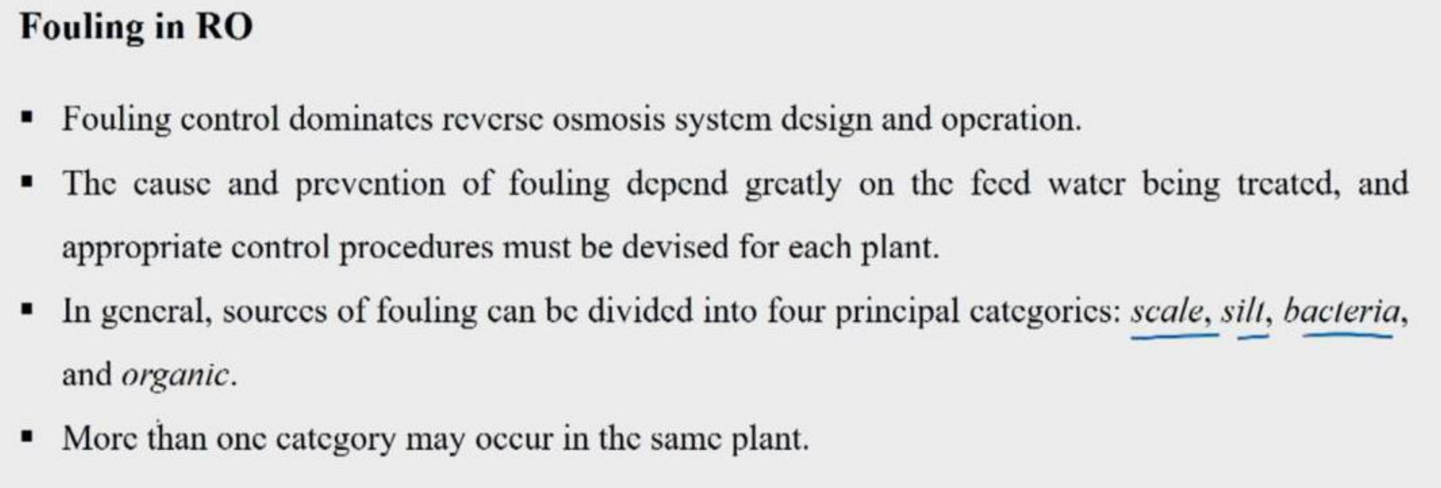
Miscellaneous Applications of RO:

- RO can be used for the recovery of valuable products from wastewater streams.
- Some specific applications include treatment of electroplating rinse waters to recover metals, in which the treated water attains suitability for reuse.
- Removal of metals from cooling tower blowdown water (which has a high TDS and 15-20 ppm chromates).
- Purification of pulp and paper industry effluents.

Fouling in RO

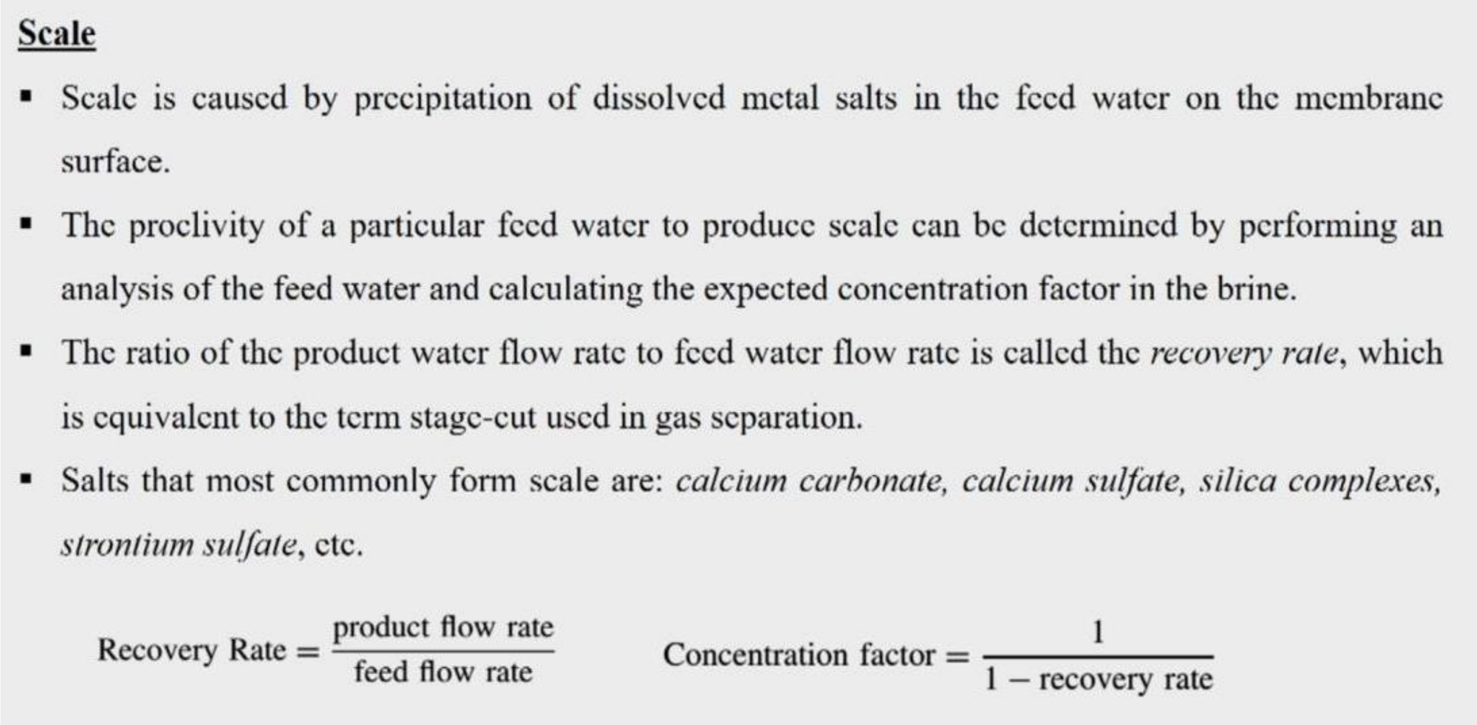
- Generally, fouling is the accumulation of undesired deposits on the membrane surface or inside the membrane pores, causing decrease of permeation flux and salt rejection.
- Membrane fouling is the main cause of permeant flux decline and loss of product quality in reverse osmosis systems.





Fouling in RO

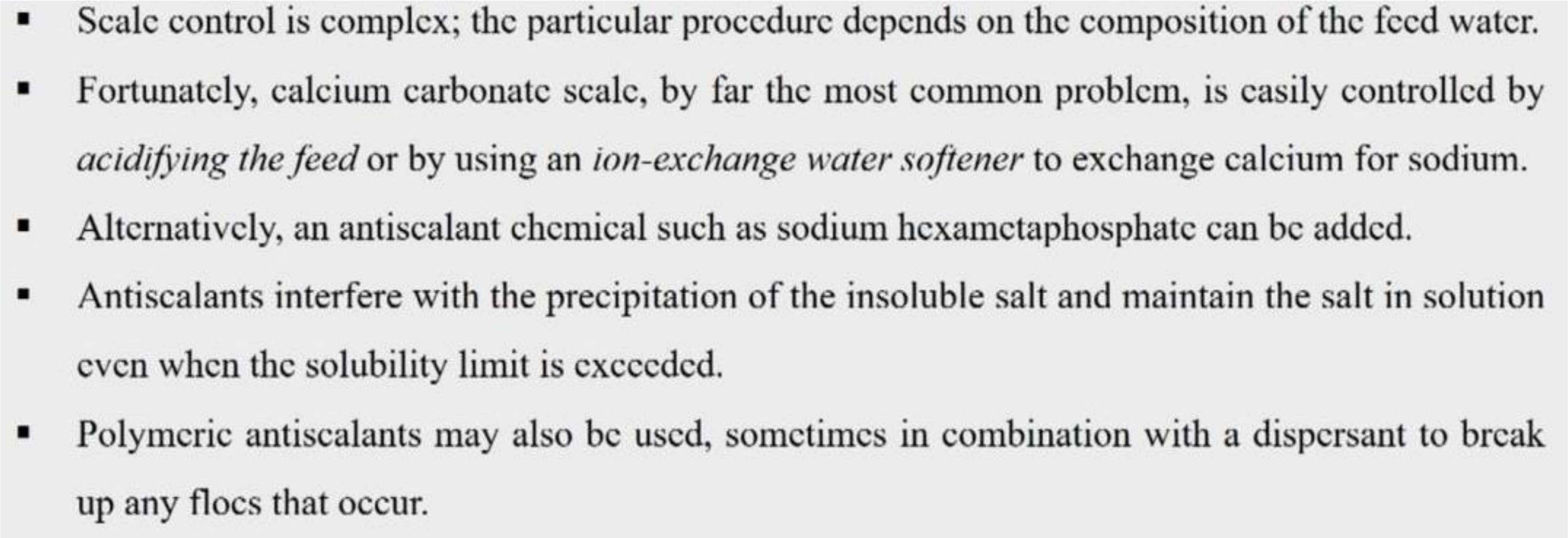
- Fouling control dominates reverse osmosis system design and operation.
- The cause and prevention of fouling depend greatly on the feed water being treated, and appropriate control procedures must be devised for each plant.
- In general, sources of fouling can be divided into four principal categories: *scale*, *silt*, *bacteria*, and *organic*.
- More than one category may occur in the same plant.



Scale

- Scale is caused by precipitation of dissolved metal salts in the feed water on the membrane surface.
- The proclivity of a particular feed water to produce scale can be determined by performing an analysis of the feed water and calculating the expected concentration factor in the brine.
- The ratio of the product water flow rate to feed water flow rate is called the *recovery rate*, which is equivalent to the term stage-cut used in gas separation.
- Salts that most commonly form scale are: *calcium carbonate, calcium sulfate, silica complexes, strontium sulfate*, etc.

$$\text{Recovery Rate} = \frac{\text{product flow rate}}{\text{feed flow rate}} \qquad \text{Concentration factor} = \frac{1}{1 - \text{recovery rate}}$$



- Scale control is complex; the particular procedure depends on the composition of the feed water.
- Fortunately, calcium carbonate scale, by far the most common problem, is easily controlled by *acidifying the feed* or by using an *ion-exchange water softener* to exchange calcium for sodium.
- Alternatively, an antiscalant chemical such as sodium hexametaphosphate can be added.
- Antiscalants interfere with the precipitation of the insoluble salt and maintain the salt in solution even when the solubility limit is exceeded.
- Polymeric antiscalants may also be used, sometimes in combination with a dispersant to break up any flocs that occur.

Silt

- Silt is formed by suspended particulates of all types that accumulate on the membrane surface.
- Typical sources of silt are organic colloids, iron corrosion products, precipitated iron hydroxide, algae, and fine particulate matter
- A good predictor of the likelihood of a particular feed water to produce fouling by silt is the ***silt density index (SDI)*** of the feed water.

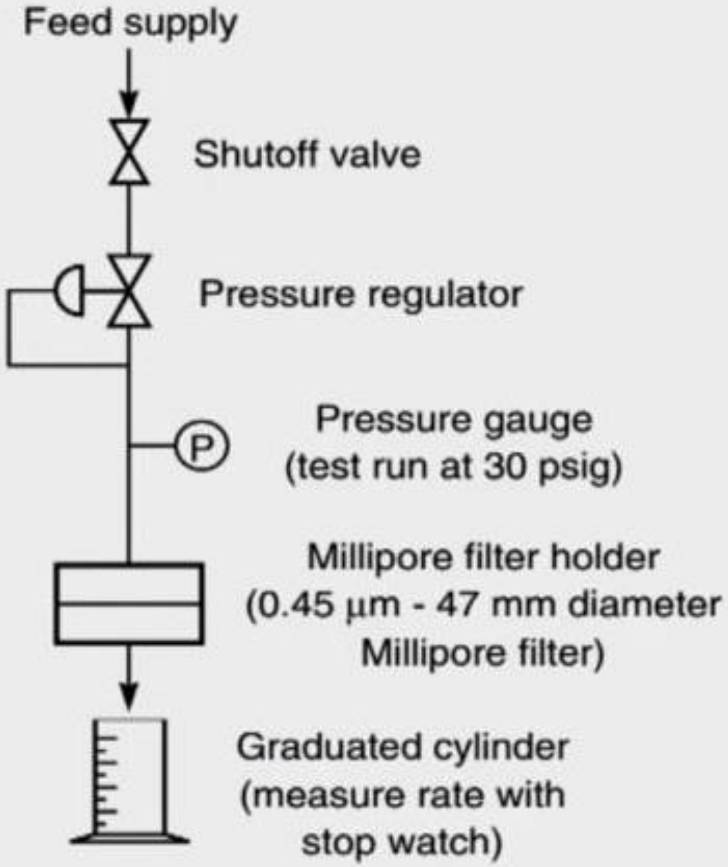


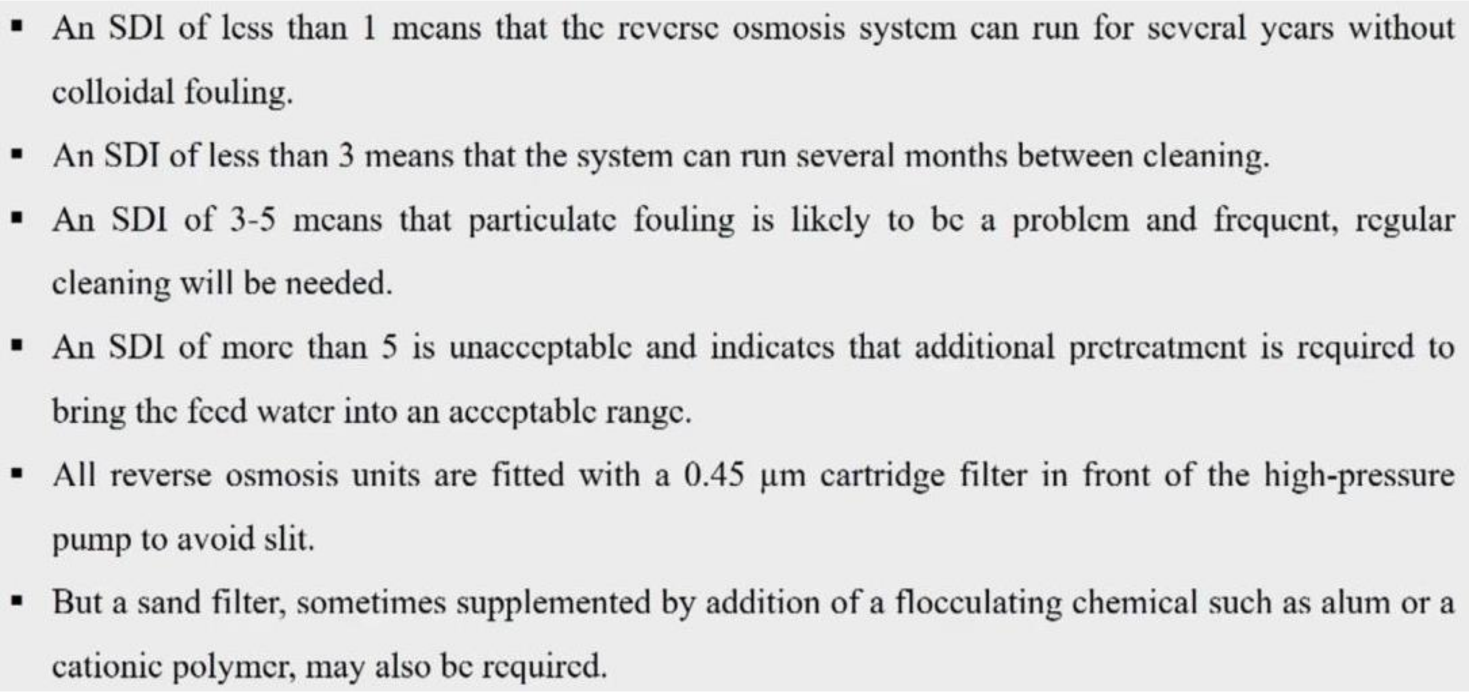
Fig. The slit density index (SDI) test

$$SDI = \frac{1 - t_i/t_f}{T} \times 100 \tag{48}$$

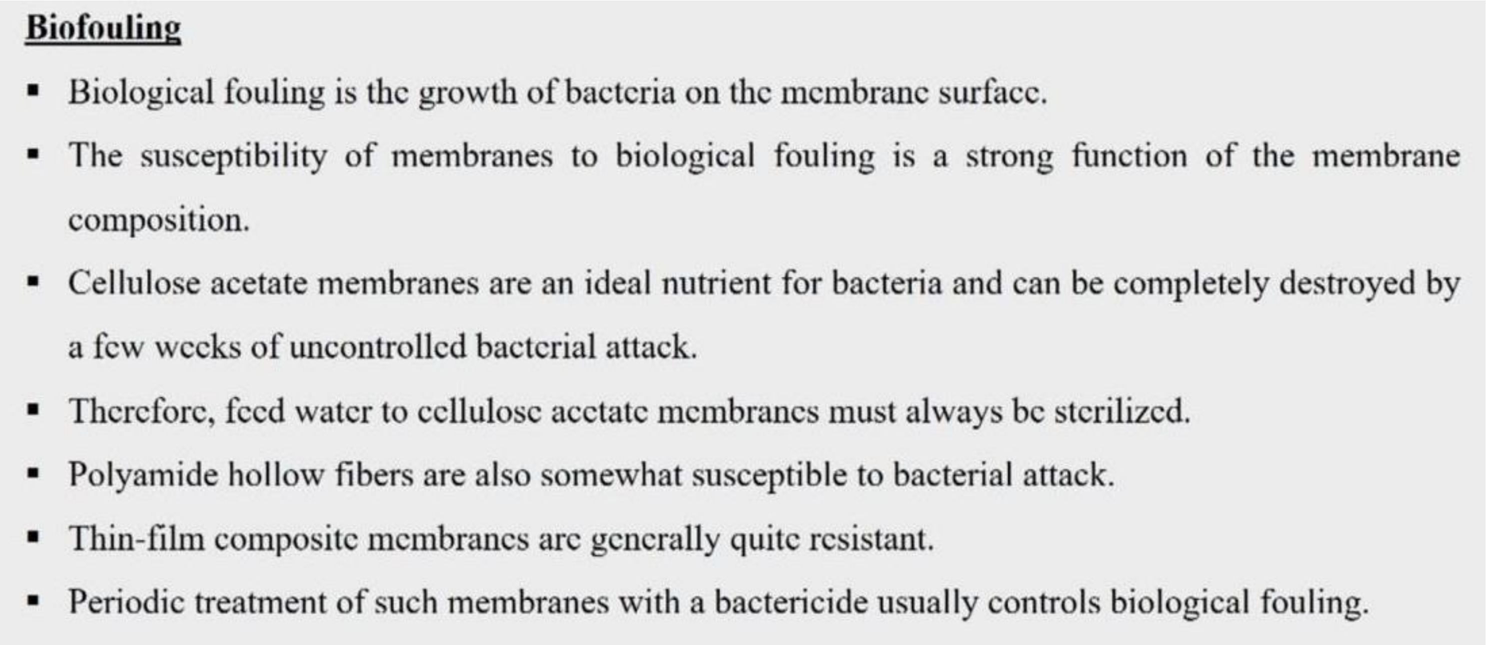
where, t_i is the time initially required to collect a sample of volume V, t_f is the time required to collect the same volume V at the end of the test, and T is the time interval. Typically, SDI is based on constant T of 15 min and is reported as SDI_{15}. For long term operations, SDI_{15} below 3 is recommended [146]. Unfortunately, SDI is not based on a filtration model and does not quantify the colloids. Also, its applicability is limited to colloids with size $> 0.45\,\mu\mathrm{m}$. The modified fouling index (MFI) has been introduced (ASTM D8002–15) in order to quantify the particle concentration and the flux decline. It is based on the mechanism of cake filtration and is defined as follows [146]:

$$MFI = \frac{\mu I}{2\Delta p S^2} \tag{49}$$

where, I is the cake resistivity and S is the active filtration area. Again, the applicability of MFI is limited to colloids with size $> 0.45\,\mu\mathrm{m}$.

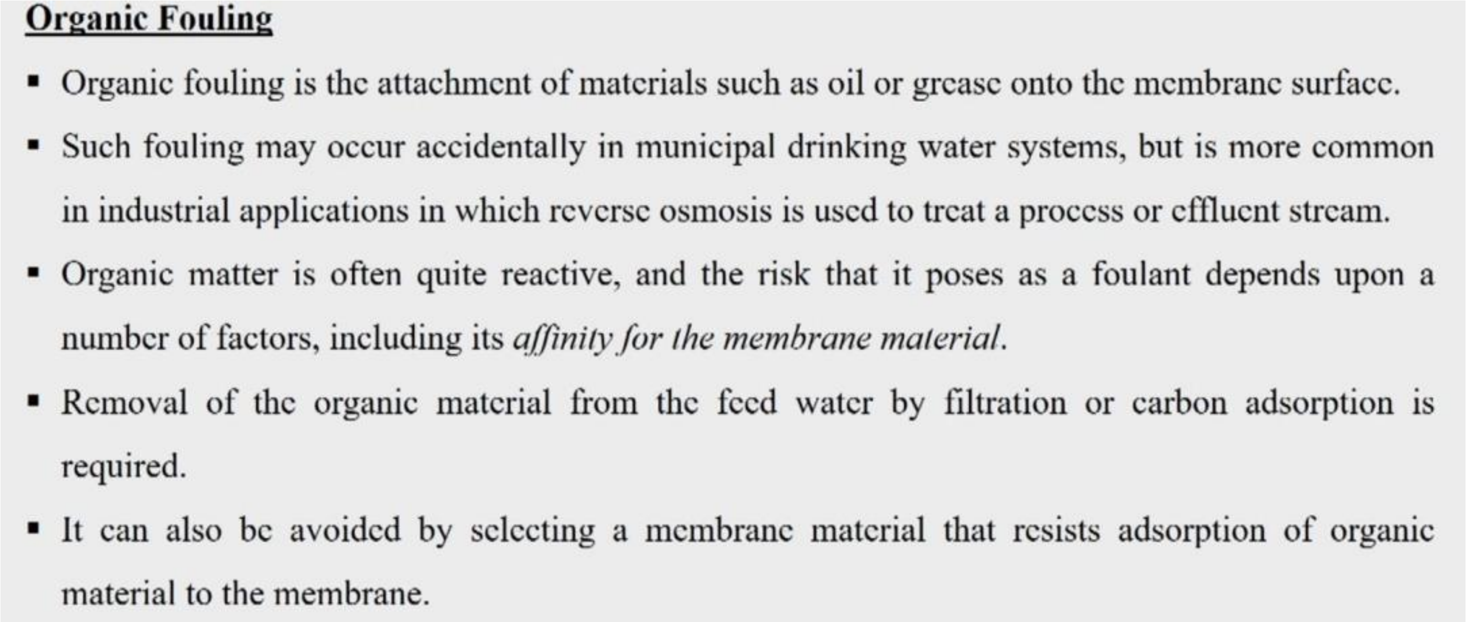


- An SDI of less than 1 means that the reverse osmosis system can run for several years without colloidal fouling.
- An SDI of less than 3 means that the system can run several months between cleaning.
- An SDI of 3-5 means that particulate fouling is likely to be a problem and frequent, regular cleaning will be needed.
- An SDI of more than 5 is unacceptable and indicates that additional pretreatment is required to bring the feed water into an acceptable range.
- All reverse osmosis units are fitted with a 0.45 µm cartridge filter in front of the high-pressure pump to avoid slit.
- But a sand filter, sometimes supplemented by addition of a flocculating chemical such as alum or a cationic polymer, may also be required.



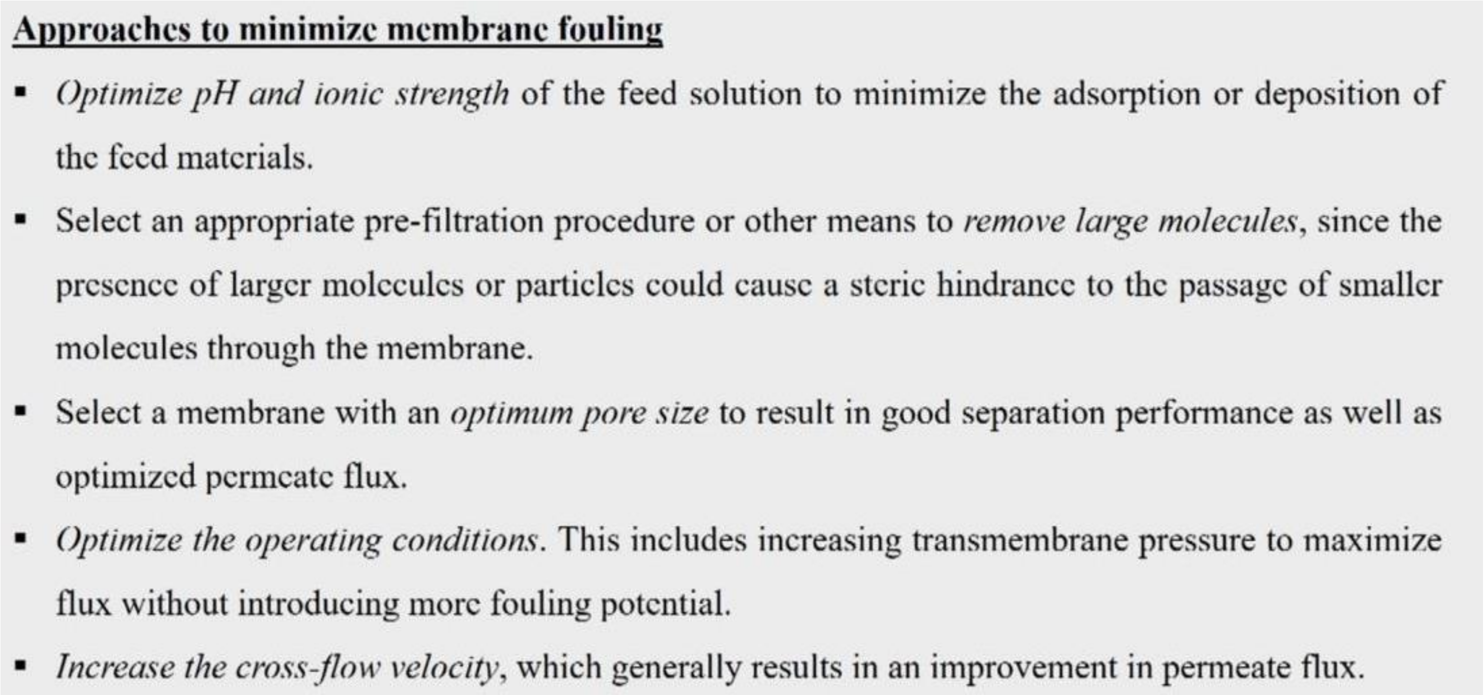
Biofouling

- Biological fouling is the growth of bacteria on the membrane surface.
- The susceptibility of membranes to biological fouling is a strong function of the membrane composition.
- Cellulose acetate membranes are an ideal nutrient for bacteria and can be completely destroyed by a few weeks of uncontrolled bacterial attack.
- Therefore, feed water to cellulose acetate membranes must always be sterilized.
- Polyamide hollow fibers are also somewhat susceptible to bacterial attack.
- Thin-film composite membranes are generally quite resistant.
- Periodic treatment of such membranes with a bactericide usually controls biological fouling.



Organic Fouling

- Organic fouling is the attachment of materials such as oil or grease onto the membrane surface.
- Such fouling may occur accidentally in municipal drinking water systems, but is more common in industrial applications in which reverse osmosis is used to treat a process or effluent stream.
- Organic matter is often quite reactive, and the risk that it poses as a foulant depends upon a number of factors, including its *affinity for the membrane material*.
- Removal of the organic material from the feed water by filtration or carbon adsorption is required.
- It can also be avoided by selecting a membrane material that resists adsorption of organic material to the membrane.



Approaches to minimize membrane fouling

- *Optimize pH and ionic strength* of the feed solution to minimize the adsorption or deposition of the feed materials.
- Select an appropriate pre-filtration procedure or other means to *remove large molecules*, since the presence of larger molecules or particles could cause a steric hindrance to the passage of smaller molecules through the membrane.
- Select a membrane with an *optimum pore size* to result in good separation performance as well as optimized permeate flux.
- *Optimize the operating conditions*. This includes increasing transmembrane pressure to maximize flux without introducing more fouling potential.
- *Increase the cross-flow velocity*, which generally results in an improvement in permeate flux.

Pressure retarded osmosis (PRO)

- In a typical PRO process, water permeates spontaneously across the semi-permeable membrane from the feed into the pressurized salty water.
- This is caused by the *chemical potential gradient* across the membrane.
- The volume and hydraulic pressure of the diluted salty water are consequently increased by this process.
- This enables the generation of electricity when releasing the pressurized water through a hydro-turbine.

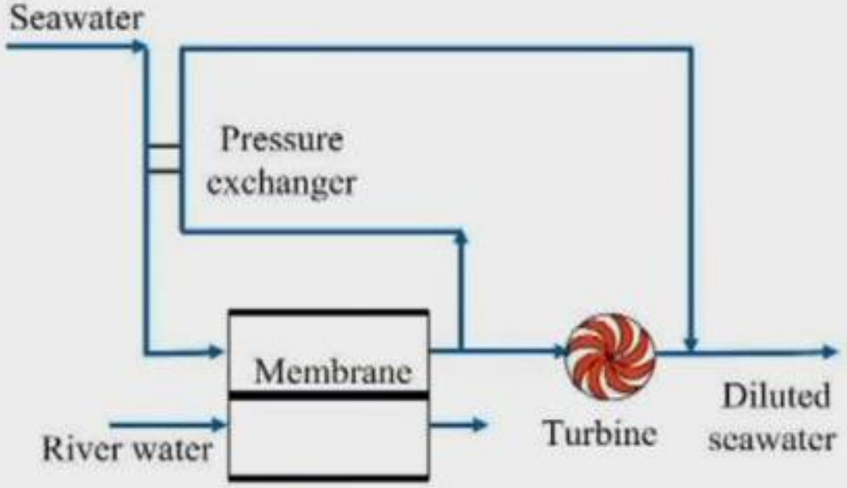


Fig. Operational principle of the pressure retarded osmosis (PRO) process

Courtesy: Aamer Ali et al., Appl. Sci. 2017, 7, 1026.

Pressure retarded osmosis (PRO)

- The water flow at a pressure $\Delta p < \Delta\pi$ can be presented as:

$$J_w = A\,(\Delta\pi - \Delta p)$$

where A (m s^{-1} bar^{-1}) is the intrinsic water permeability coefficient of the membrane.

- The power E (Watt or J/s) per unit membrane area is given by:

$$E = J_w\,.\,\Delta p = A\,(\Delta\pi - \Delta p)\,\Delta p$$

- The power is at maximum ($E = E_{max}$) at $dE/d(\Delta p) = 0$, So $\Delta p = 0.5\,\Delta\pi$, which implies that

$$E_{max} = A/4\,.\,\pi r^2$$

- The above equation signifies the effect of osmotic pressure on the maximum power.

Courtesy: Gang Han et al.Progress in Polymer Science 51 (2015) 1–27.

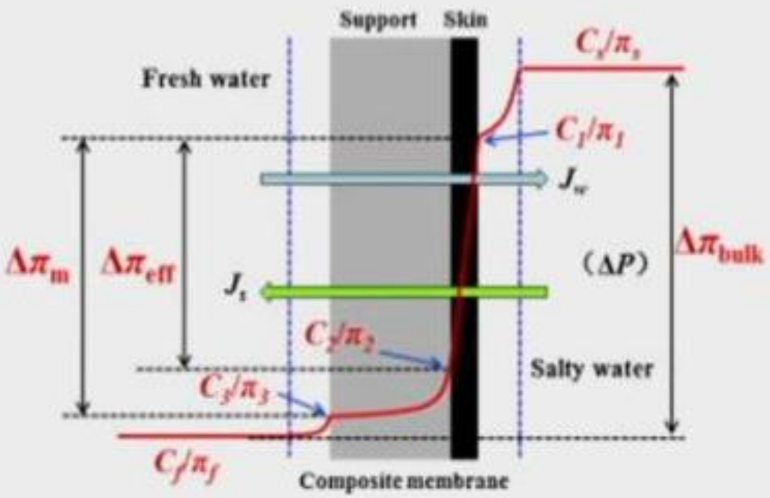
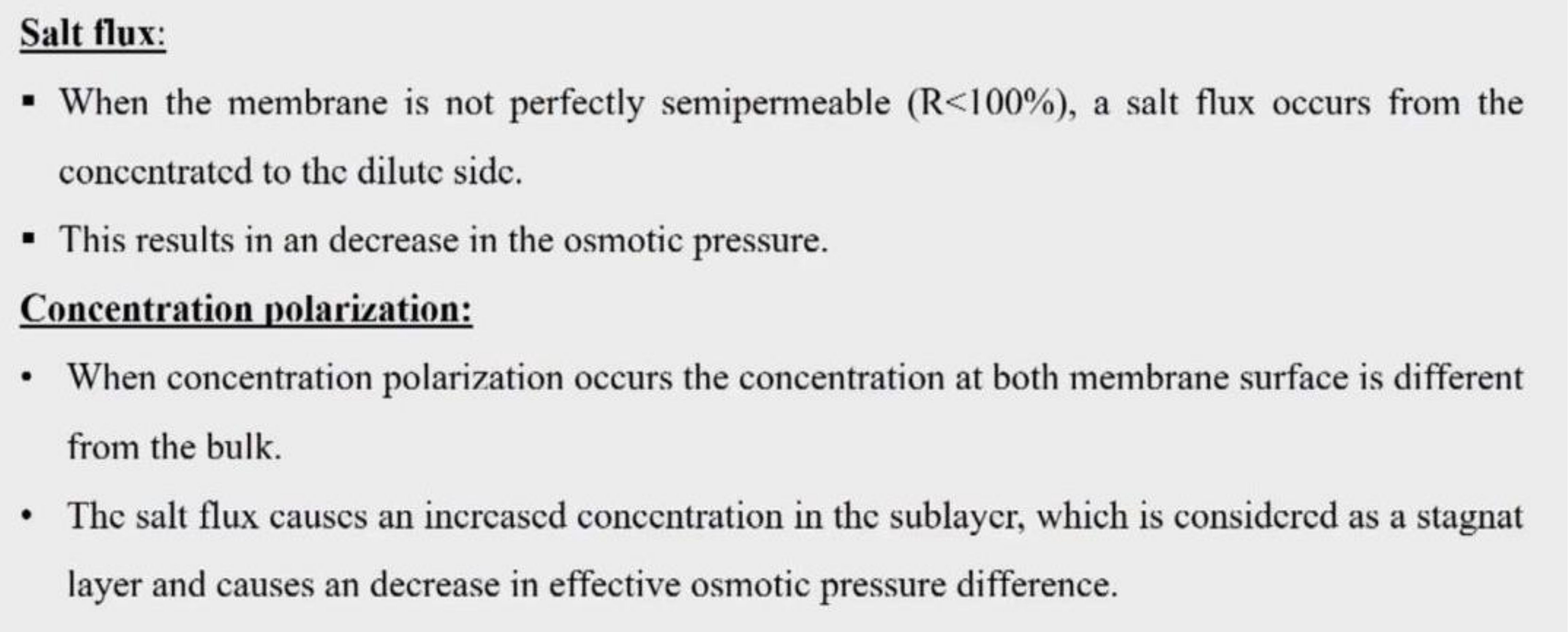


Fig. Schematic of the salt concentration and osmotic pressure profiles across an asymmetric composite membrane operated in PRO.

C_s and C_f − salt concentrations of the bulk salty water and fresh water solutions, respectively. $C1$− salt concentration at the interface between the salty water and the membrane selective layer. $C2$− salt concentration at the interface between the membrane support and the active layer. $C3$− salt concentration at the interface of the fresh water and the membrane substrate. $\Delta\pi bulk$− osmotic pressure different between the bulk fresh water and salty water. $\Delta\pi m$− osmotic pressure different across the membrane. $\Delta\pi eff$− effective osmotic pressure gradient across the membrane selective layer.



Salt flux:

- When the membrane is not perfectly semipermeable (R<100%), a salt flux occurs from the concentrated to the dilute side.
- This results in an decrease in the osmotic pressure.

Concentration polarization:

- When concentration polarization occurs the concentration at both membrane surface is different from the bulk.
- The salt flux causes an increased concentration in the sublayer, which is considered as a stagnat layer and causes an decrease in effective osmotic pressure difference.

Pressure retarded osmosis (PRO)

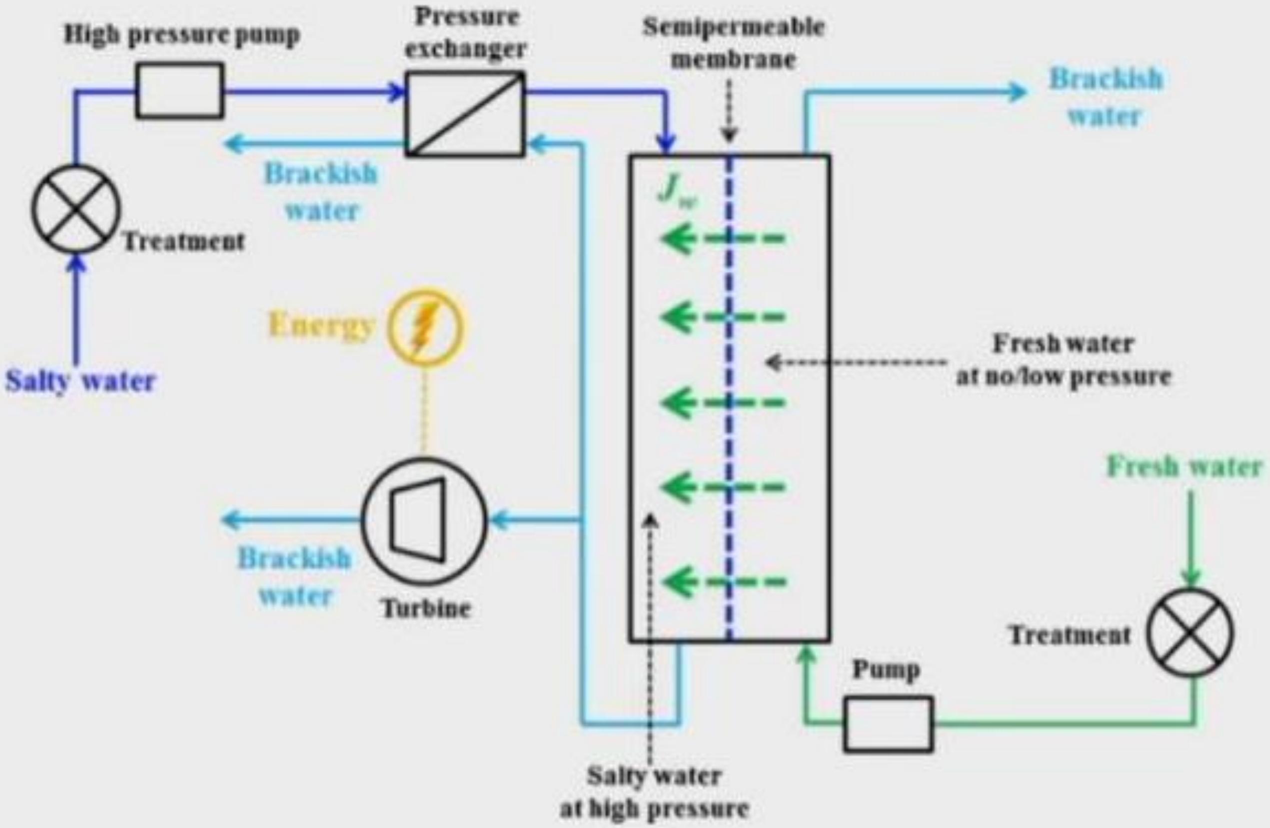
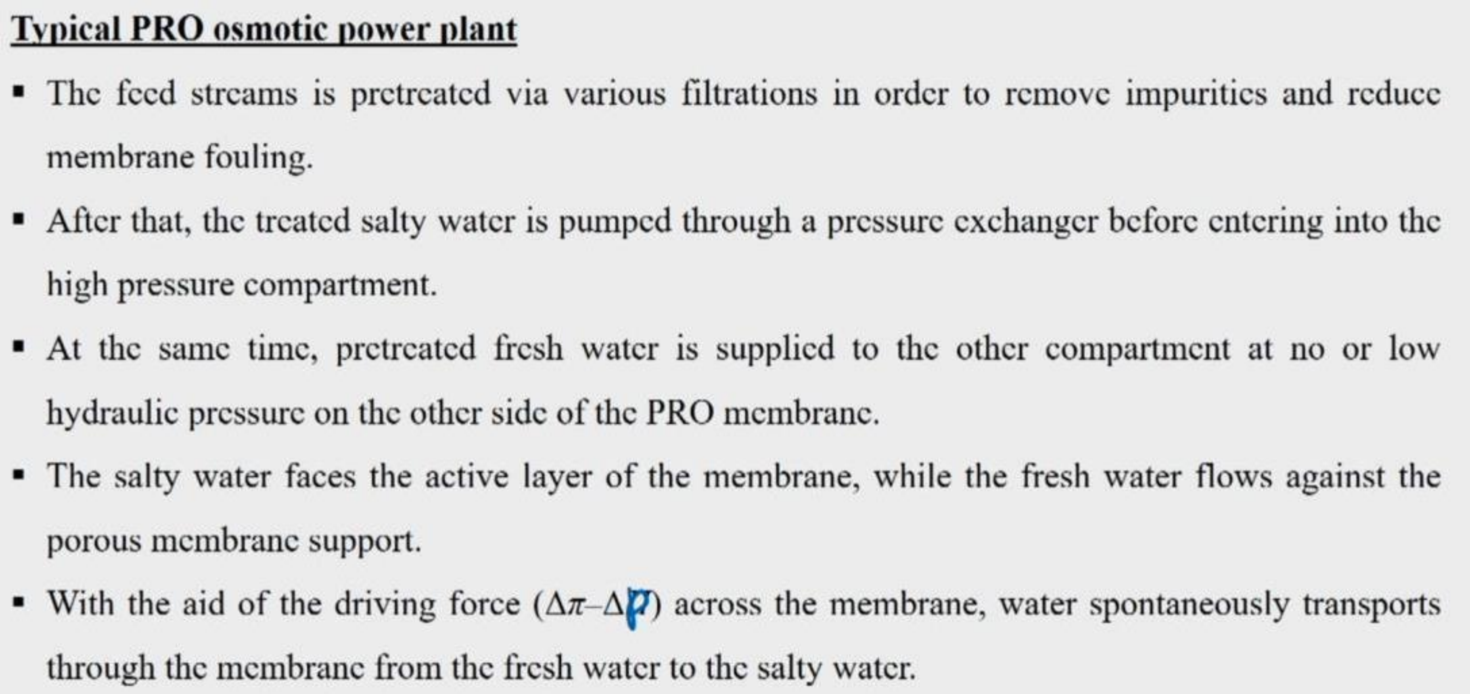
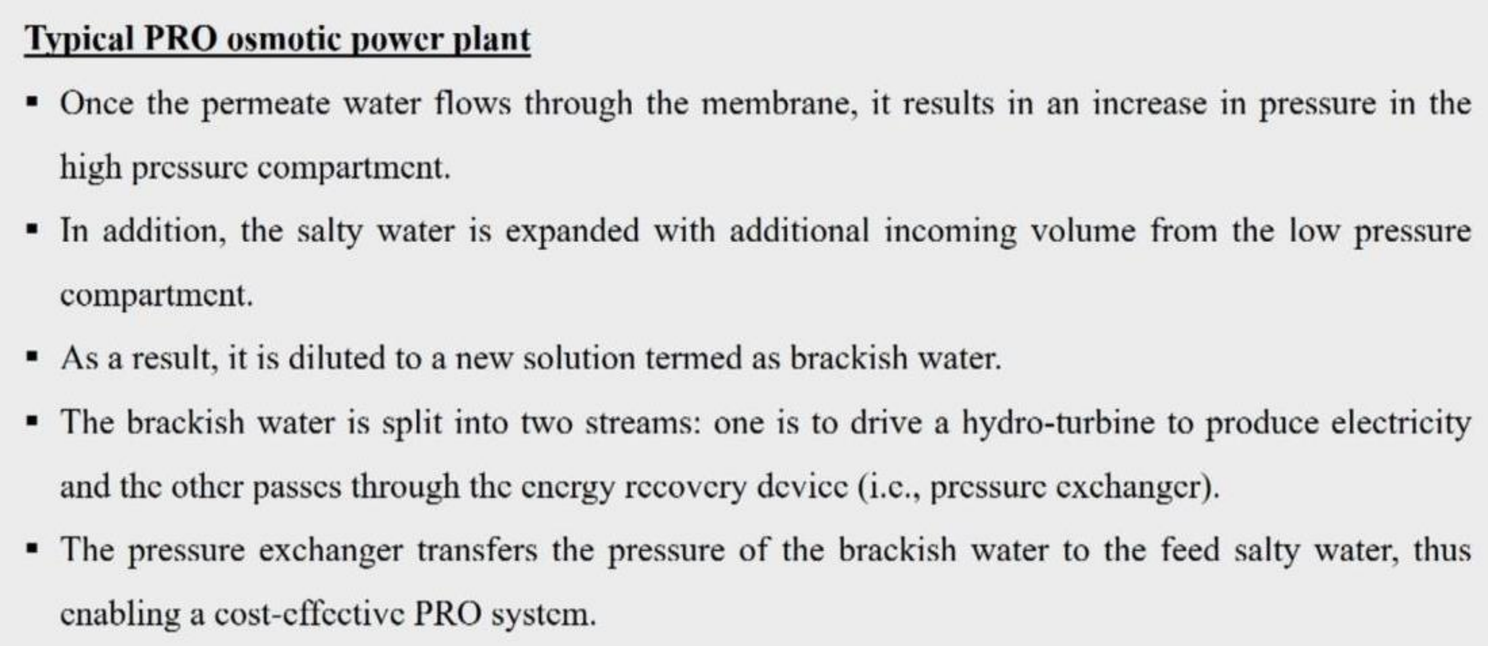


Fig. Schematic diagram of a typical PRO osmotic power plant with continuous and steady state flow



Typical PRO osmotic power plant

- The feed streams is pretreated via various filtrations in order to remove impurities and reduce membrane fouling.
- After that, the treated salty water is pumped through a pressure exchanger before entering into the high pressure compartment.
- At the same time, pretreated fresh water is supplied to the other compartment at no or low hydraulic pressure on the other side of the PRO membrane.
- The salty water faces the active layer of the membrane, while the fresh water flows against the porous membrane support.
- With the aid of the driving force ($\Delta\pi - \Delta P$) across the membrane, water spontaneously transports through the membrane from the fresh water to the salty water.



Typical PRO osmotic power plant

- Once the permeate water flows through the membrane, it results in an increase in pressure in the high pressure compartment.
- In addition, the salty water is expanded with additional incoming volume from the low pressure compartment.
- As a result, it is diluted to a new solution termed as brackish water.
- The brackish water is split into two streams: one is to drive a hydro-turbine to produce electricity and the other passes through the energy recovery device (i.e., pressure exchanger).
- The pressure exchanger transfers the pressure of the brackish water to the feed salty water, thus enabling a cost-effective PRO system.

Forward Osmosis

- Forward osmosis is the process of spontaneous water diffusion across a semi-permeable forward osmosis membrane in response to a difference in solute concentrations (i.e. osmotic pressures) on either side of the semi-permeable membrane.
- In forward osmosis, the water molecules from saline water move through the semipermeable membrane toward the draw solution, which is maintained at a higher concentration than the feed solution.
- FO mainly uses osmotic pressure gradient and not the hydraulic pressure gradient.

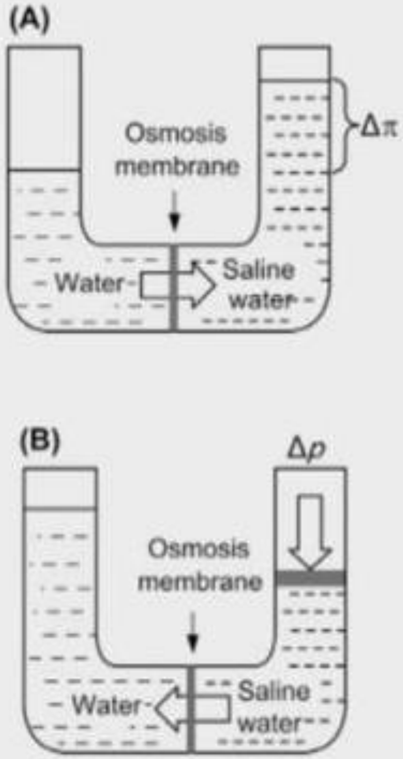


Fig. Operation principle of (A) forward osmosis and (B) reverse osmosis

Principle

- In forward osmosis (FO) water molecules spontaneously move from water to saline water through the semipermeable membrane.
- The liquid level of the saline water will be elevated until the liquid level pressure difference between the two sides is the same as the osmotic pressure difference ($\Delta p = \Delta\pi$).
- If the water is replaced by the draw solution with lower chemical potential, water molecules spontaneously will move from saline water to draw solution through the semipermeable membrane which is still the FO process.
- The feature of forward osmosis is the process driving force just coming from chemical potential difference but no outer force.

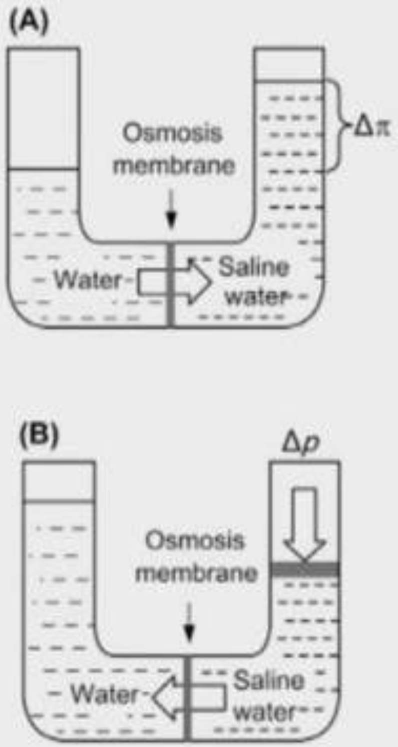
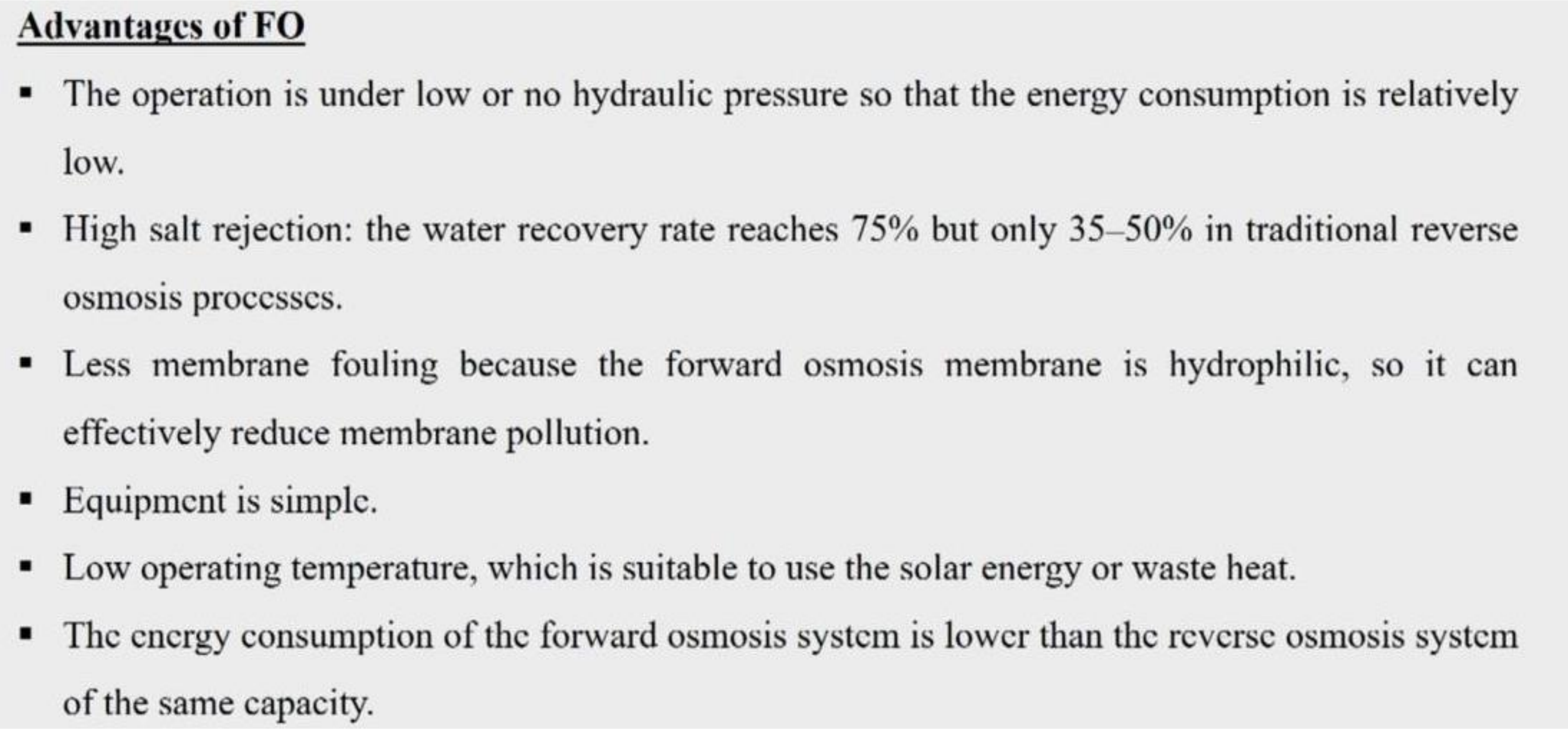


Fig. Operation principle of (A) forward osmosis and (B) reverse osmosis



Advantages of FO

- The operation is under low or no hydraulic pressure so that the energy consumption is relatively low.
- High salt rejection: the water recovery rate reaches 75% but only 35–50% in traditional reverse osmosis processes.
- Less membrane fouling because the forward osmosis membrane is hydrophilic, so it can effectively reduce membrane pollution.
- Equipment is simple.
- Low operating temperature, which is suitable to use the solar energy or waste heat.
- The energy consumption of the forward osmosis system is lower than the reverse osmosis system of the same capacity.

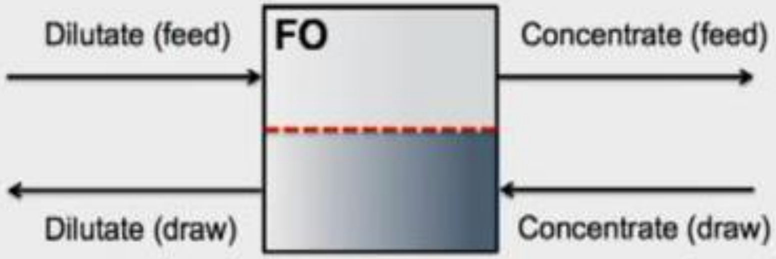
Applications of FO

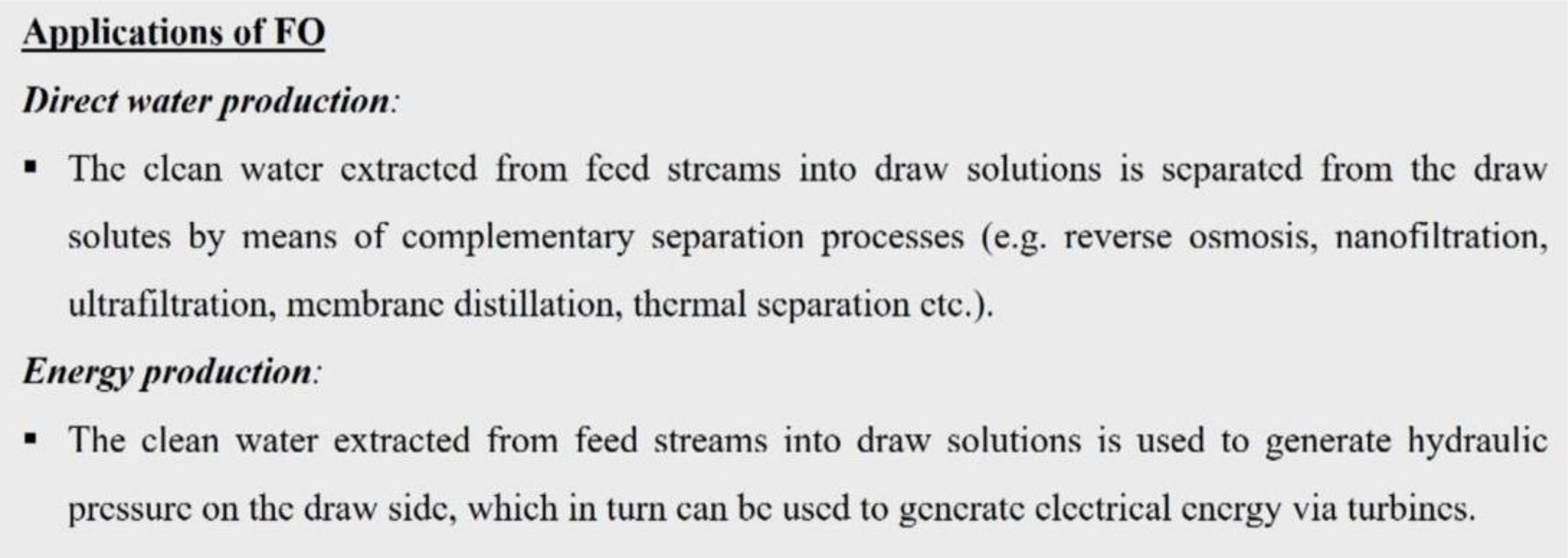
***Concentration*:**

- Water is extracted by forward osmosis processes from specific feed streams.
- Continuous extraction of clean water from said feed solutions will result in volume reduction, which in effect concentrates solutes and any other components.
- This process is also known as *dewatering*.

***Dilution (indirect water production)*:**

- Water is extracted from feed streams by forward osmosis processes into a given draw solution.
- Continuous extraction of clean water into the draw solution will result in volume increase, which in effect dilutes solutes and any other components.





Applications of FO

***Direct water production*:**

- The clean water extracted from feed streams into draw solutions is separated from the draw solutes by means of complementary separation processes (e.g. reverse osmosis, nanofiltration, ultrafiltration, membrane distillation, thermal separation etc.).

***Energy production*:**

- The clean water extracted from feed streams into draw solutions is used to generate hydraulic pressure on the draw side, which in turn can be used to generate electrical energy via turbines.

Forward Osmosis: Applications

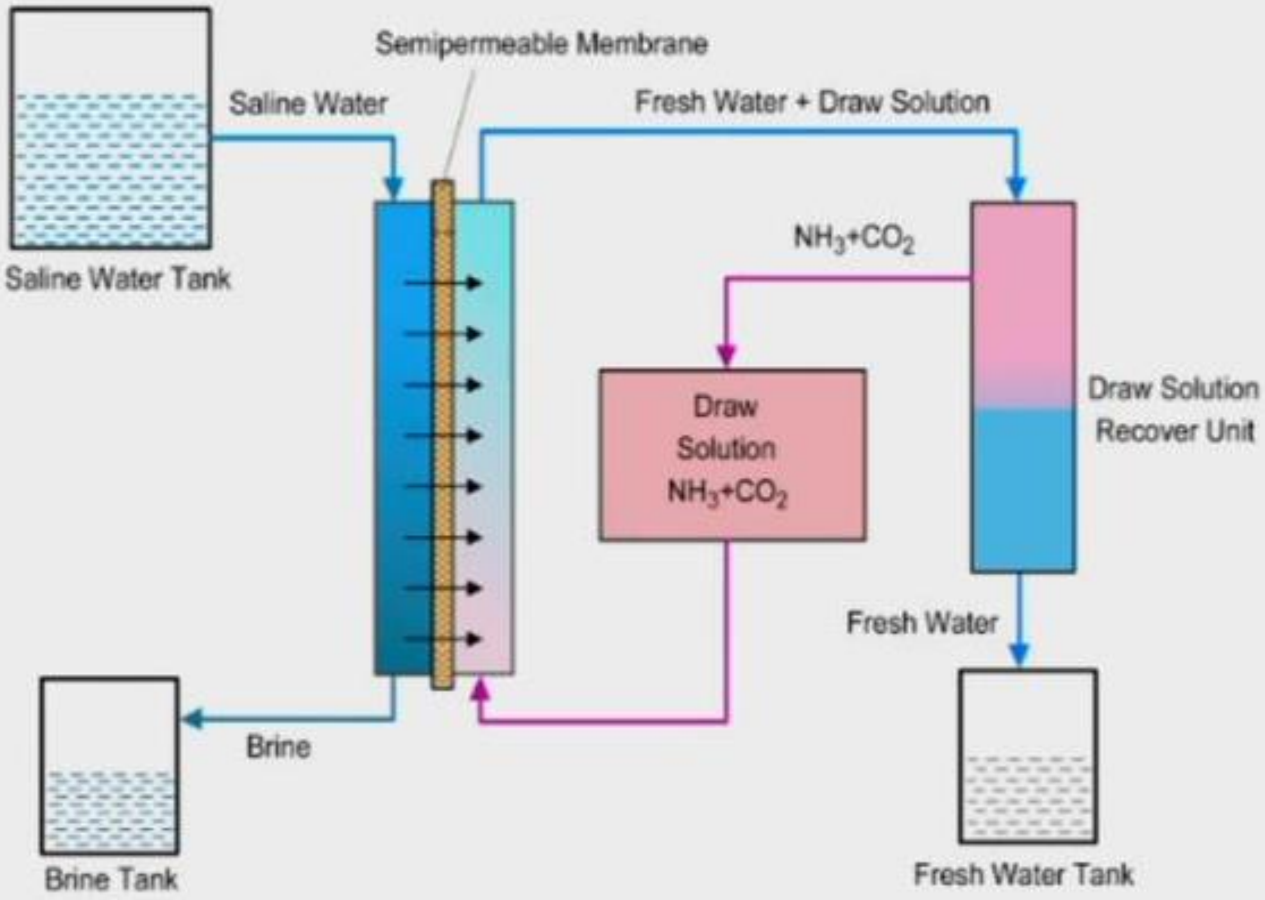


Fig. Forward osmosis unit using NH_3-CO_2 as draw solution

Forward Osmosis: Applications

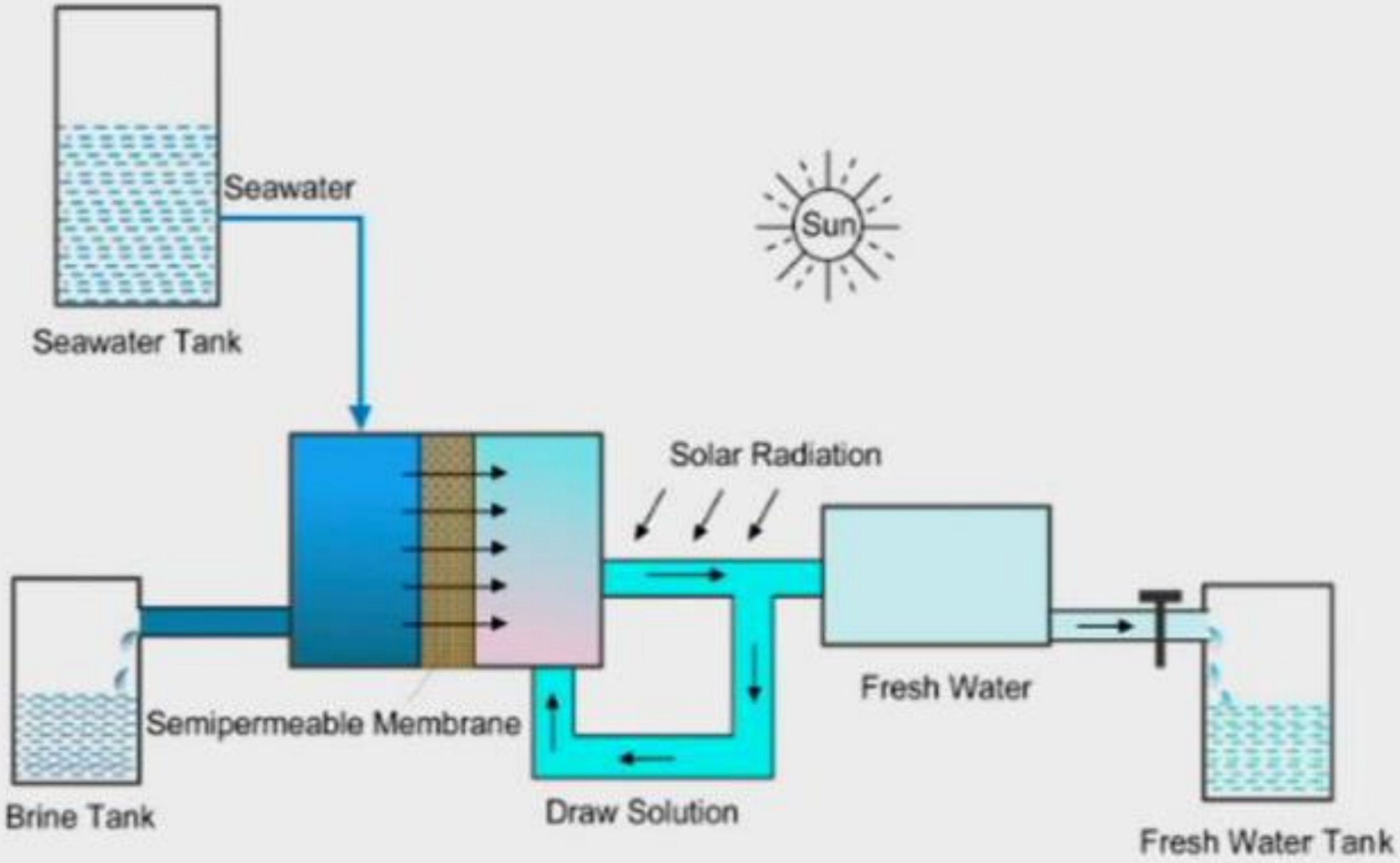


Fig. Forward osmosis unit driven by solar energy

Table 1. Overview of the traditional classification of draw solutions (DSs) in forward osmosis (FO) process.

Categories	Draw Solutes	Recovery Methods	Ref.
Inorganic compounds	NaCl	reverse osmosis (RO)	[33]
	inorganic fertilizer	direct use	[45]
	potassium sulfate (K_2SO_4)	RO	[33]
	sodium nitrate ($NaNO_3$)	direct use	[46]
	aluminum sulfate ($Al_2(SO_4)_3$)	precipitation	[47]
	magnesium sulfate ($MgSO_4$), copper sulfate ($CuSO_4$)	precipitation	[48,49]
Organic compounds	Switchable polarity solvent (SPS)	RO	[50]
	sodium polyacrylate (PAA-Na)	ultrafiltration (UF), membrane distillation (MD)	[51,52]
	CO_2-responsive polymers (PDMAEMA)	UF	[53]
	poly(sodium styrene-4-sulfonate-co-*N*-isopropylacrylamide) (PSSS-PNIPAM)	MD	[54]
	poly (aspartic acid sodium salt)	MD	[55]
	N,*N*-dimethylcyclohexylamine ($N(Me)_2Cy$)	heating	[56]
	1-Cyclohexylpiperidine (CHP)	heating	[57]
	Micellar solution	UF	[58]
	oxalic acid complexes with Fe/Cr/Na	nanofiltration (NF)	[59]
	2-Methylimidazole compounds	MD	[60]
	trimethylamine–carbon dioxide	heating	[61]
	glucose, fructose	RO	[62–64]
	polyelectrolyte incorporated with triton-x114	MD	[65]
	dimethyl ether	heating with solar energy	[66]
	poly(4-styrenesulfonic acid-co-maleic acid)	NF	[67]
Functional nanoparticles	Super hydrophilic nanoparticles	UF	[40]
	hydrophilic superparamagnetic nanoparticles	magnetic separation	[68]
	magnetic core-hydrophilic shell nanosphere	magnetic separation	[69]
	thermoresponsive Magnetic Nanoparticle	magnetic separation	[42]
	dextran-coated MNPs	magnetic separation	[36]
	hyperbranched polyglycerol coated MNPs	magnetic separation	[70]

Table 2. Overview of DSs based on the types of energy used in recovery process.

Categories	Recovery Methods	Draw Solutes
Direct use	Without recovery	Saccharides (glucose, fructose) [72,73], fertilizer [20,46], liquid fertilizer [74], sodium lignin sulfonate (NaLS) [75]
Chemical energy	Precipitation	$Al_2(SO_4)_3$ [47,76], $MgSO_4$ [49], $CuSO_4$ [77]
Waste heat	Heating	Sulfur dioxide (SO_2) [78], ammonia and carbon dioxide (NH_3-CO_2) [79]
	heating	*N*,*N*-dimethylcyclohexylamine ($N(Me)_2Cy$) [56], 1-Cyclohexylpiperidine (CHP) [57], trimethylamine-carbon dioxide ($N(CH_3)_2$-CO_2) [61], switchable polarity solvents [50], ionic polymer hydrogels with thermal responsive units [80]
	phase separation	Upper critical solution temperature (UCST) ionic liquid [81], ammonium iodide salts [82], lower critical solution temperature (LCST) ionic liquid [83], thermally responsive polyionic liquid hydrogels [84–86], thermosensitive copolymer [54], ionic hydrogels [34], thermo-sensitive polyelectrolyte [87], phase transition materials [88], CO_2 switchable dual responsive polymers [89,90], thermosensitive polymer coated magnetic nanoparticles [38], gas-responsive cationic microgels [91]
	MD	2-Methylimidazole salt [60], Na^+-functionalized carbon quantum dots (Na-CQDs) [92], dendrimer [93], poly (aspartic acid sodium salt) [55], multi-charged oxalic acid complexes [94]
Electric energy	RO	Inorganic salt (NaCl [95,96], $MgCl_2$ [95], KNO_3 [33]), organic ionic salts [97], glucose and sucrose miscible liquids [63]
	NF	divalent metal salt (Na_2SO_4, $MgSO_4$) [98], EDTA sodium salt [21], metal complexes [27,59,99], poly (4-styrenesulfonic acid-co-maleic acid) [69], novel carboxyethyl amine sodium salts [100], organic phosphonate salts [101]
	UF	Thermosensitive polyelectrolyte [102], surface modified MNPs [37,39], phosphatic surfactant [103], micellar solution [58,104], sodium polyacrylate [52], carboxylate polyelectrolyte [105], natural polymer-based cationic polyelectrolyte [106]
	MF	Thermo-responsive copolymers [107]
Solar energy	Irradiating	Bifunctional polymer hydrogel layers [108], graphene gels [109], thermo-responsive nanoparticles [110], composite hydrogel monoliths containing thermoplastic polyurethane microfibers [111], composite hydrogels (carbon particles and sodium acrylate-isopropylacrylamide) (SA-NIPAM) [112,113], composite hydrogels based on graphene and SA-NIPAM [114], dimethyl ether [66]
Magnetic field energy	Magnetic separation	Functionalized MNPs [37], citrate-coated MNPs [115], PAA-Na coated-MNPs [34,116], thermosensitive magnetic nanogels [38,42], dextran coated Fe_3O_4 magnetic nanoparticles [36], triethylene glycol-coated magnetic nanoparticles, polyacrylic acid-coated magnetic nanoparticles [37], poly(oxy-1,2-ethanediyl)-coated magnetic nanoparticles [39], poly(ethylene glycol) diacid-coated (PEG-$(COOH)_2$-coated) MNPs [39], hyperbranched polyglycerol coated MNPs [70], polyacrylic acid-coated MNPs [37,40,41]

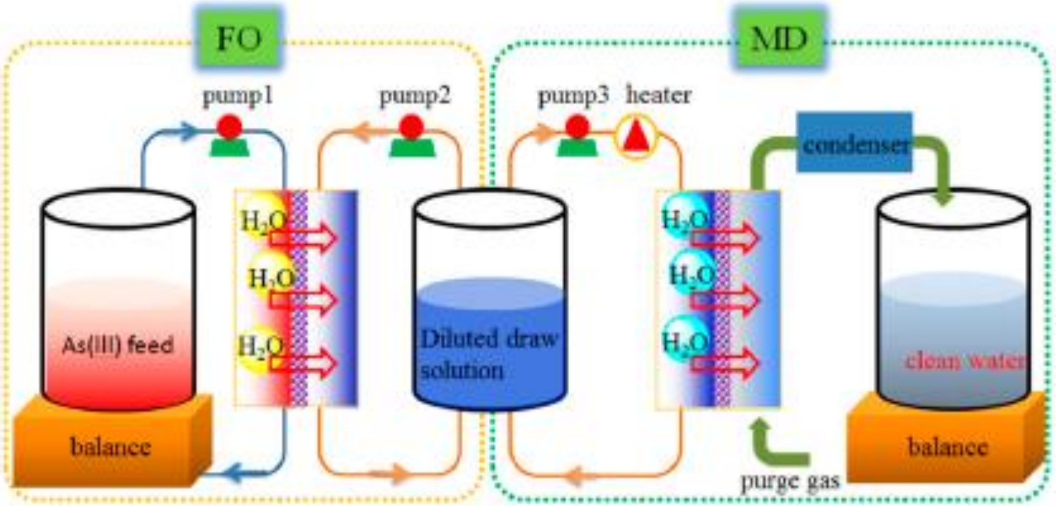


Figure 2. Schematic illustration of using a hybrid FO-MD process for wastewater treatment.

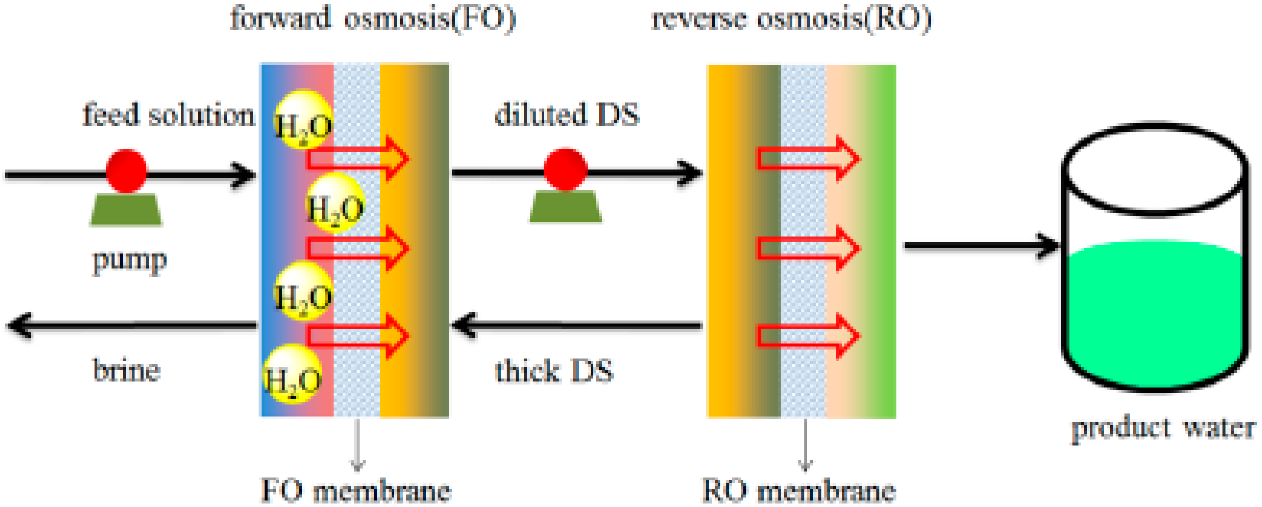
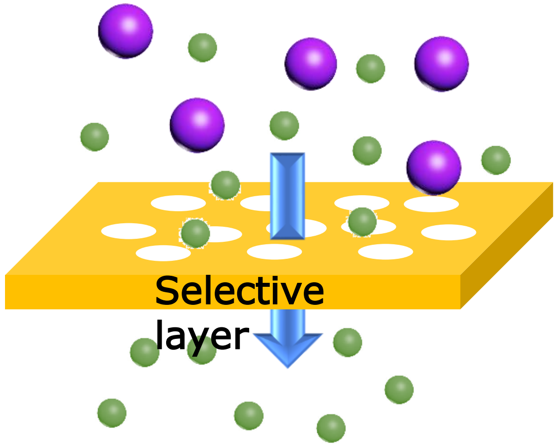


Figure 3. Schematic illustration of using a hybrid FO-RO process for desalination seawater.

PROSES PEMISAHAN

Gas separation membrane



Oleh : Indah Prihatiningtyas D.S

Gas separation

- Membrane methods of separation are modern techniques which could reduce capital investment, operating cost and process safety.
- Separation of binary gas mixtures is an important unit operation in a large number of industries to recover valuable gases and enable pollution control.
- Such separations are currently undertaken by conventional technology viz., cryogenic distillation, adsorption on solid surface and solvent absorption. Now membranes are increasingly finding application for gaseous separations and have exhibited tremendous potential.
- Large scale gas permeators have already been employed in industrial sectors in the US and some European countries.
- Membrane technology could compete as well as compliment conventional separation techniques due to its multidimensional character, which involves rapid mass transfer rate and high selectivity towards a specific gas. Inherent advantages of membrane gas separation process are as follows:

Simplicity of operation and installation.

- ❑ Feasibility under mild conditions, for eg. air separation can be carried out at lower pressure and ambient temperature rather than extreme conditions in cryogenic distillation.
- ❑ Smaller footprint and flexibility of operation due to compactness of modules with huge reduction in consumption of electricity and fuel.
- ❑ No extra agents are required as compared to corrosive and polluting amine solvents in absorption process.
- ❑ Continuous mode of operation with partial or complete recycle of retentate/permeate.
- ❑ Possibility of integration with other separation units to constitute effective hybrid processes for achieving improved economy and desired purity levels.
- ❑ Membranes can be “tailored” to adapt to a specific separation task.

Gas separation

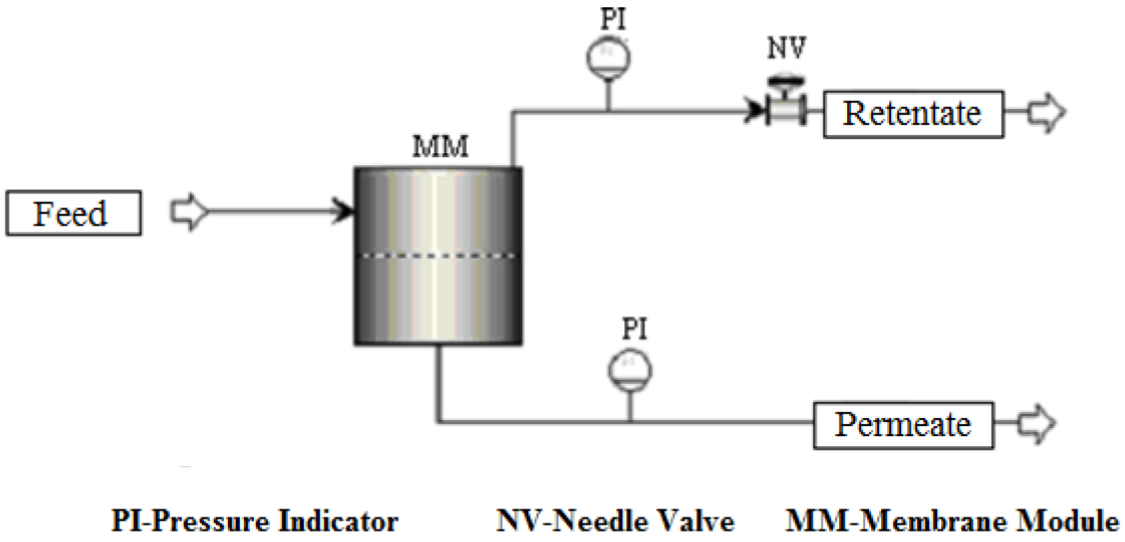


Figure 1. Schematic of Membrane Gas Separation Process

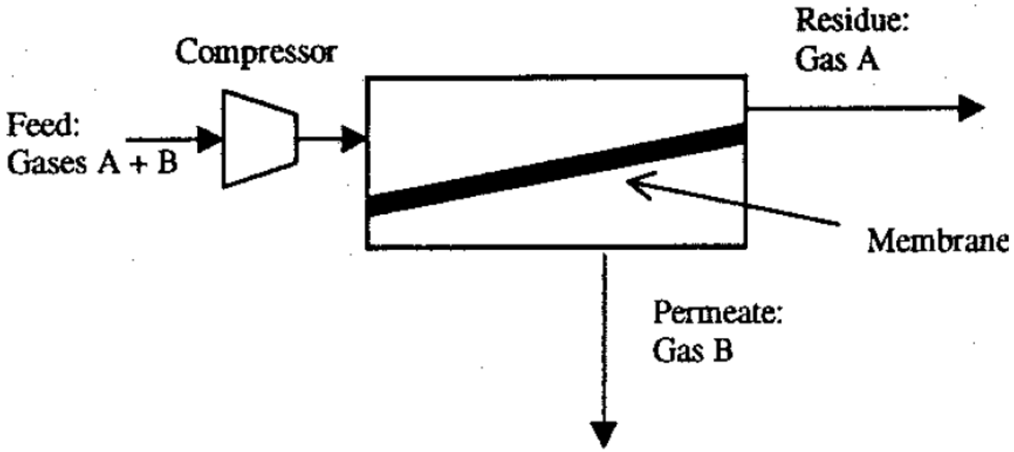


FIG. 1 A simplified illustration of a gas separation membrane system.

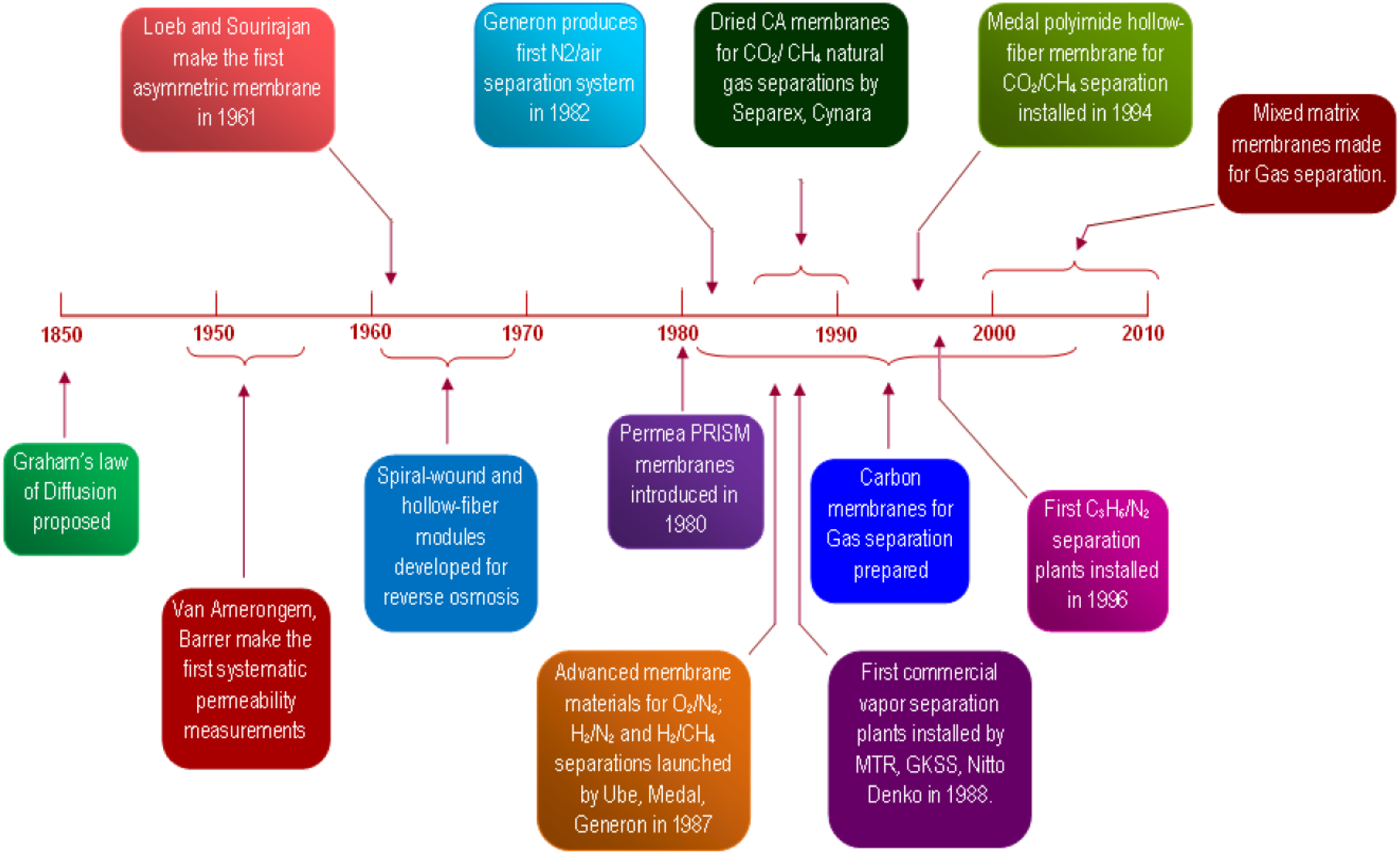


Fig. 2. Background and Milestones in Membrane Gas Separation

Table 1. Properties of Common Gases

Gas	State	Molecular weight	Kinetic diameter (Å)	Specific gravity at 70 °F (1 atm)	Critical temp (°F)	Critical pressure (psig)	Specific volume (cf/lb)
H_2	Compressed Gas	2.02	2.89	0.0696	-399.96	190.8	192
N_2	Compressed Gas	28.01	3.64	0.967	-232.4	492.9	13.8
He	Compressed Gas	4.003	2.6	0.138	-450.3	33.2	96.7
O_2	Compressed Gas	32.0	3.46	1.105	-181.1	736.9	12.1
CO_2	Liquefied Gas	44.01	3.3	1.52	87.8	1071	8.74
C_3H_6	Liquefied Gas	42.08	4.4	1.501	197.5	666.3	9.05
C_3H_8	Liquefied Gas	44.1	3.96	1.55	206.2	617.4	8.5
CH_4	Compressed Gas	16.04	3.8	0.555	-115.8	673	23.7
CO	Compressed Gas	28.01	3.76	0.97	-220.4	507.4	13.8
Ar	Compressed Gas	39.95	3.4	1.38	-188.1	710	9.7

Theory of gas permeation

- The driving force for gas separation is partial pressure gradient which is the product of total pressure and mole fraction.
- Most membranes used for gas separation are non-porous (Porous polymer membranes have a pore size ranging from 0.5 to 10 µm).

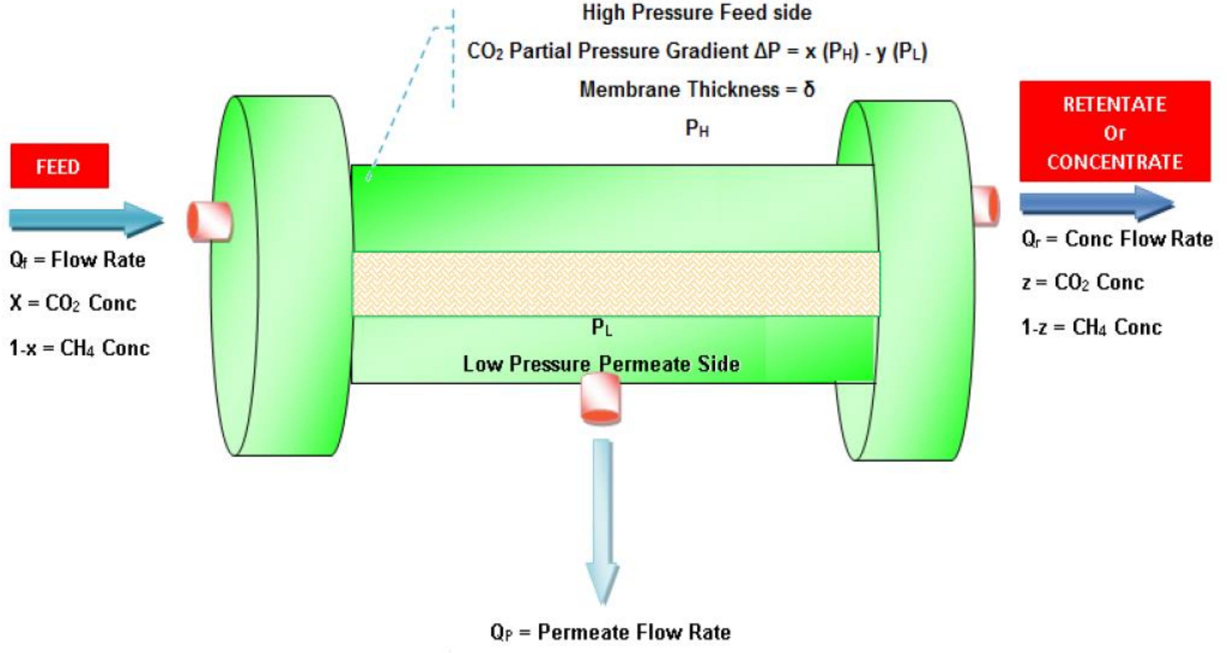
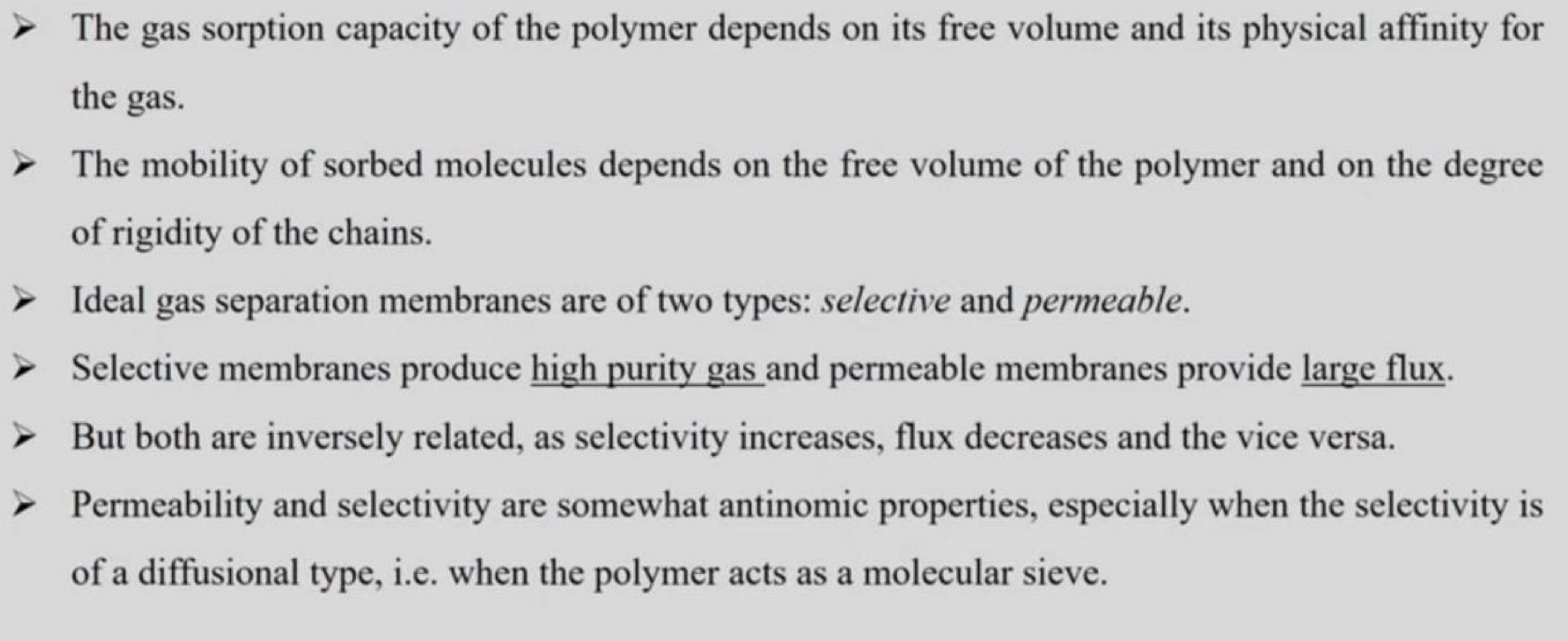
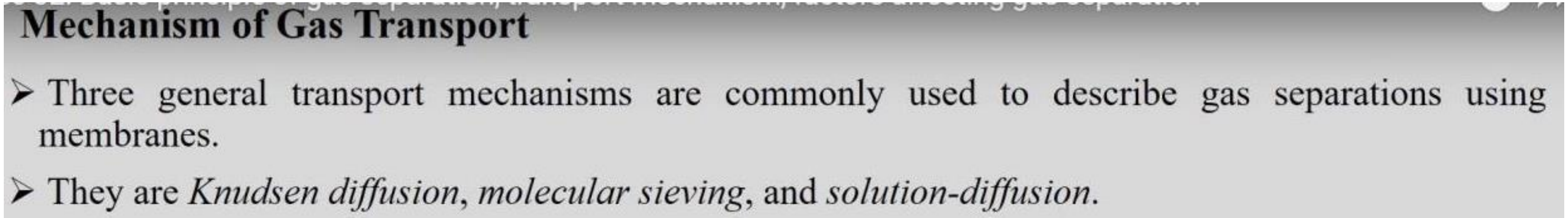


Figure 3. Principle of Gas Permeation and Separation



- The gas sorption capacity of the polymer depends on its free volume and its physical affinity for the gas.
- The mobility of sorbed molecules depends on the free volume of the polymer and on the degree of rigidity of the chains.
- Ideal gas separation membranes are of two types: *selective* and *permeable*.
- Selective membranes produce high purity gas and permeable membranes provide large flux.
- But both are inversely related, as selectivity increases, flux decreases and the vice versa.
- Permeability and selectivity are somewhat antinomic properties, especially when the selectivity is of a diffusional type, i.e. when the polymer acts as a molecular sieve.



Mechanism of Gas Transport

- Three general transport mechanisms are commonly used to describe gas separations using membranes.
- They are *Knudsen diffusion*, *molecular sieving*, and *solution-diffusion*.

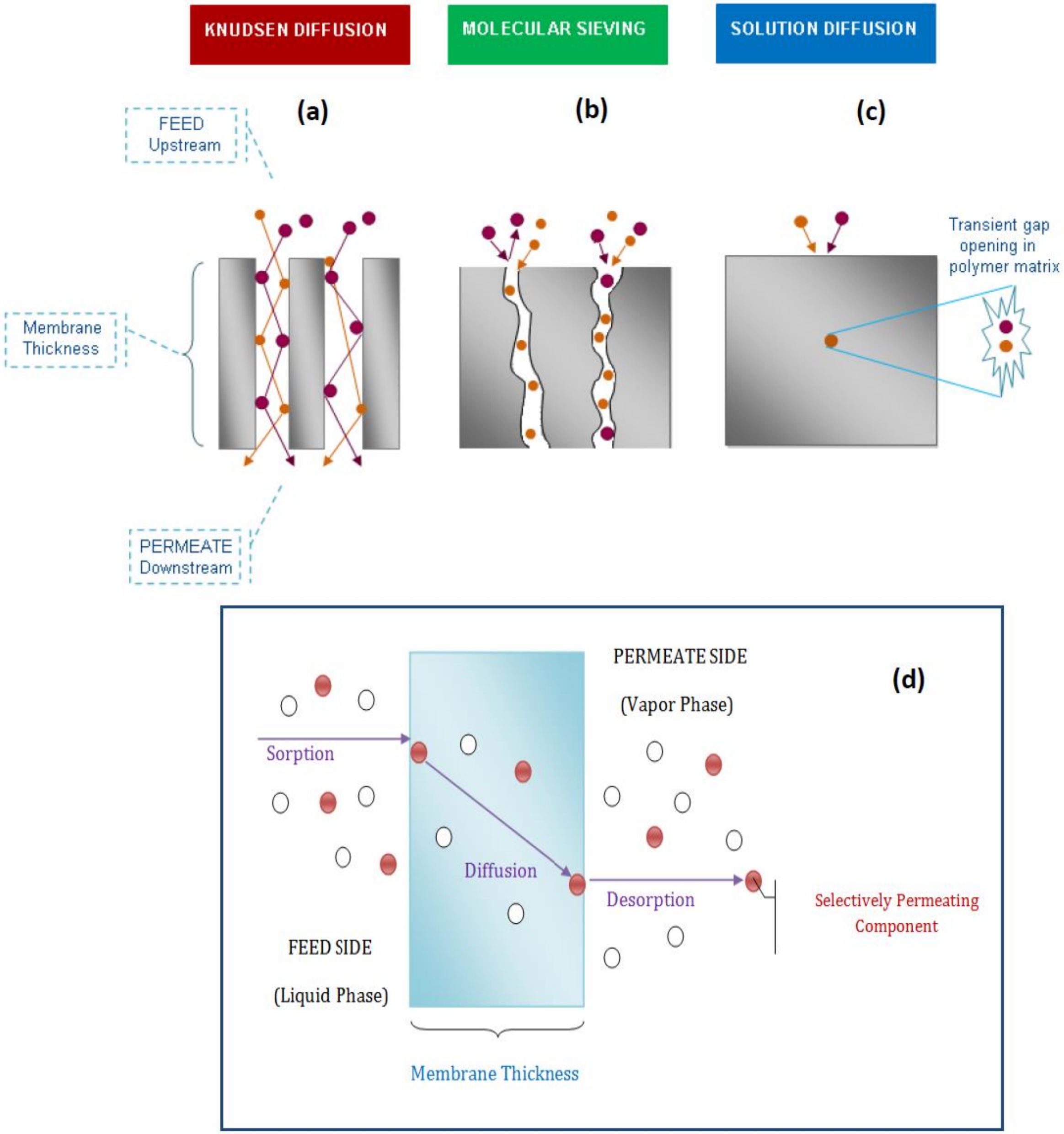
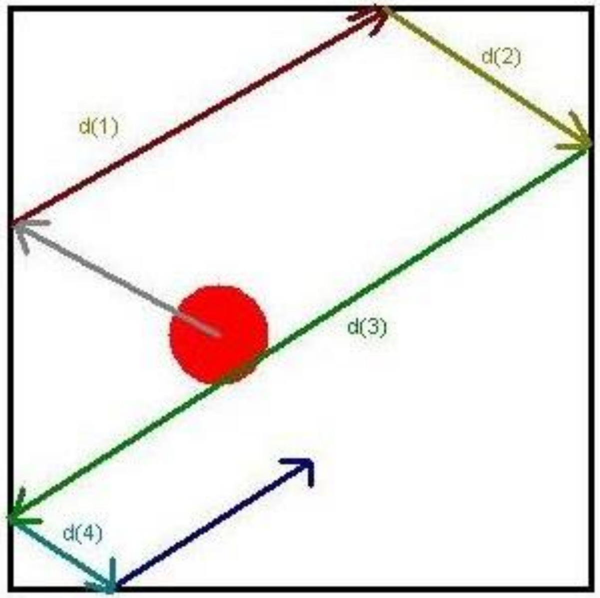


Fig. 4. Mechanisms of Gas Permeation: (a) Knudsen's Diffusion, (b) Molecular Sieving, (c) Solution-Diffusion and (d) Detailed Overview of Mass Transfer by Solution-Diffusion

Knudsen Diffusion

- Knudsen‟s diffusion principally takes place in membranes with a pore diameter in the range of 50-100Å .
- Knudsen‟s diffusion occurs in a porous membrane, whose pore sizes are smaller than the mean free path of the gas molecules .

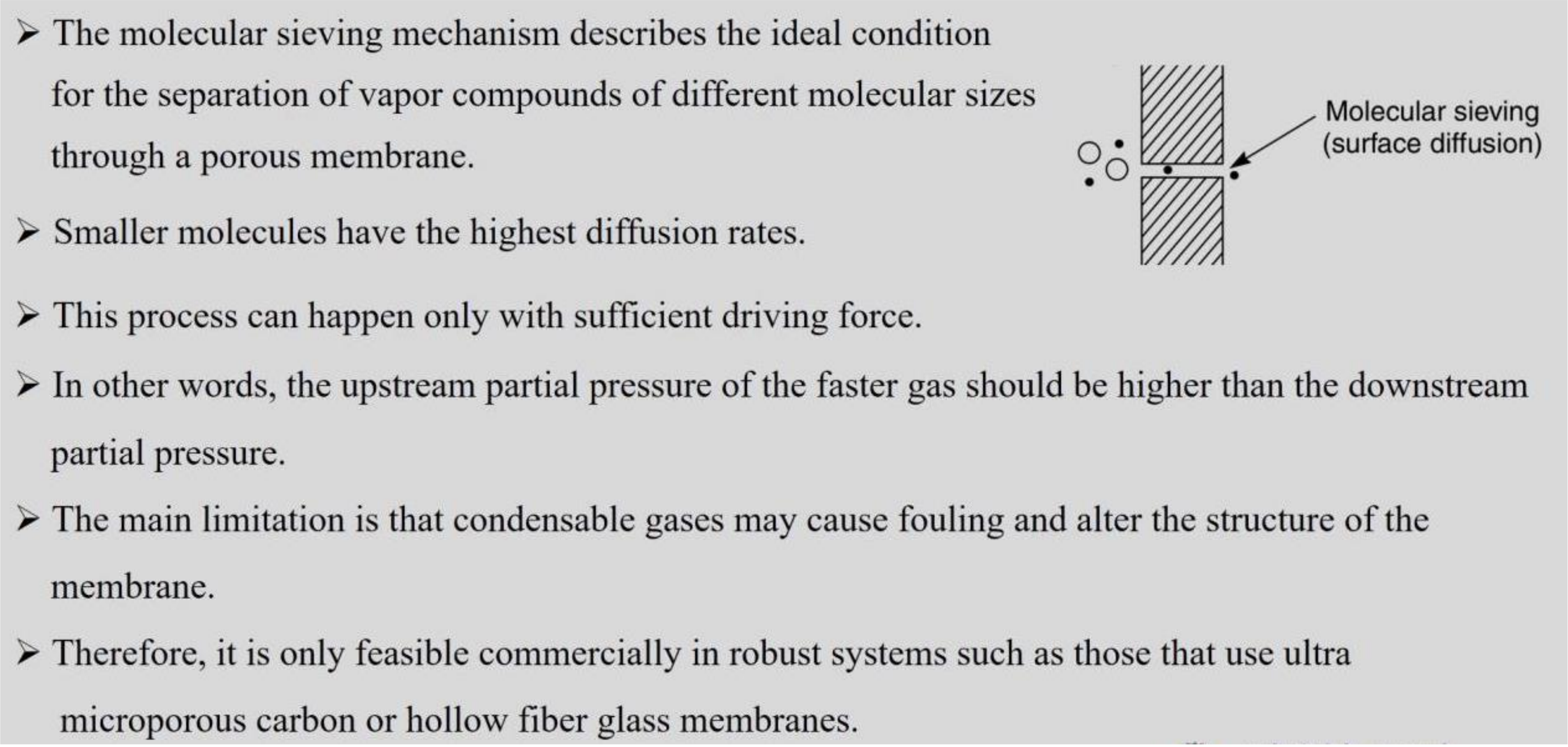


The mean free path is the average distance traveled by a moving molecule between collisions.

$\lambda=(d1+d2+d3+d4) / 4$

Molecular Sieving

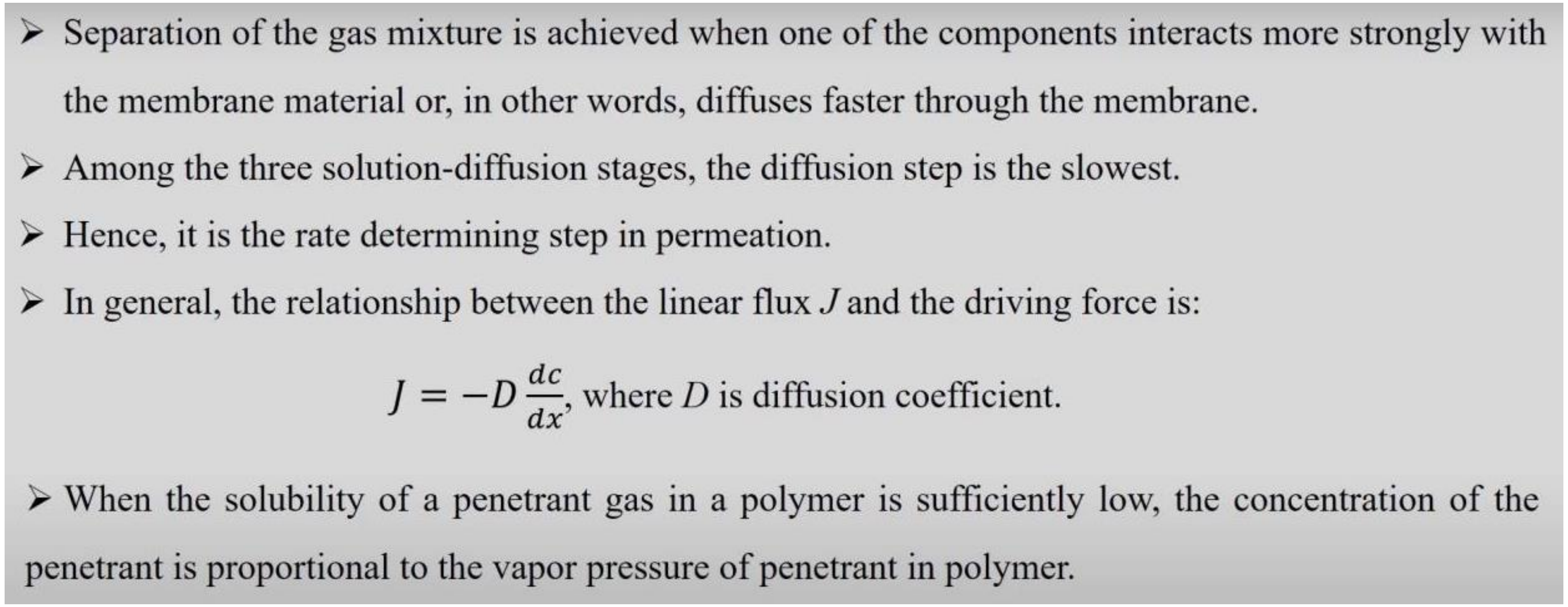
- Molecular sieving is primarily based on the precise size exclusion and shape discrimination amongst various gas molecules by the micropores of < 7Å in diameter.



- ➢ The molecular sieving mechanism describes the ideal condition for the separation of vapor compounds of different molecular sizes through a porous membrane.
- ➢ Smaller molecules have the highest diffusion rates.
- ➢ This process can happen only with sufficient driving force.
- ➢ In other words, the upstream partial pressure of the faster gas should be higher than the downstream partial pressure.
- ➢ The main limitation is that condensable gases may cause fouling and alter the structure of the membrane.
- ➢ Therefore, it is only feasible commercially in robust systems such as those that use ultra microporous carbon or hollow fiber glass membranes.

Solution-Diffusion

- Transport of gases through nonporous polymeric membranes is usually described by solution–diffusion mechanism
- Consists of three steps, (a) sorption of preferential permeate (solubility) at the upstream surface of the membrane, (b) activated diffusion through the membrane and (c) desorption at the downstream side.
- Solution-diffusion mechanism is driven by a difference in thermodynamic activities existing across the membrane and interacting forces working between membrane material and permeating molecules.
- Permeability (*P*) is the capability of a membrane to permeate gas molecules:



➢ Separation of the gas mixture is achieved when one of the components interacts more strongly with the membrane material or, in other words, diffuses faster through the membrane.

➢ Among the three solution-diffusion stages, the diffusion step is the slowest.

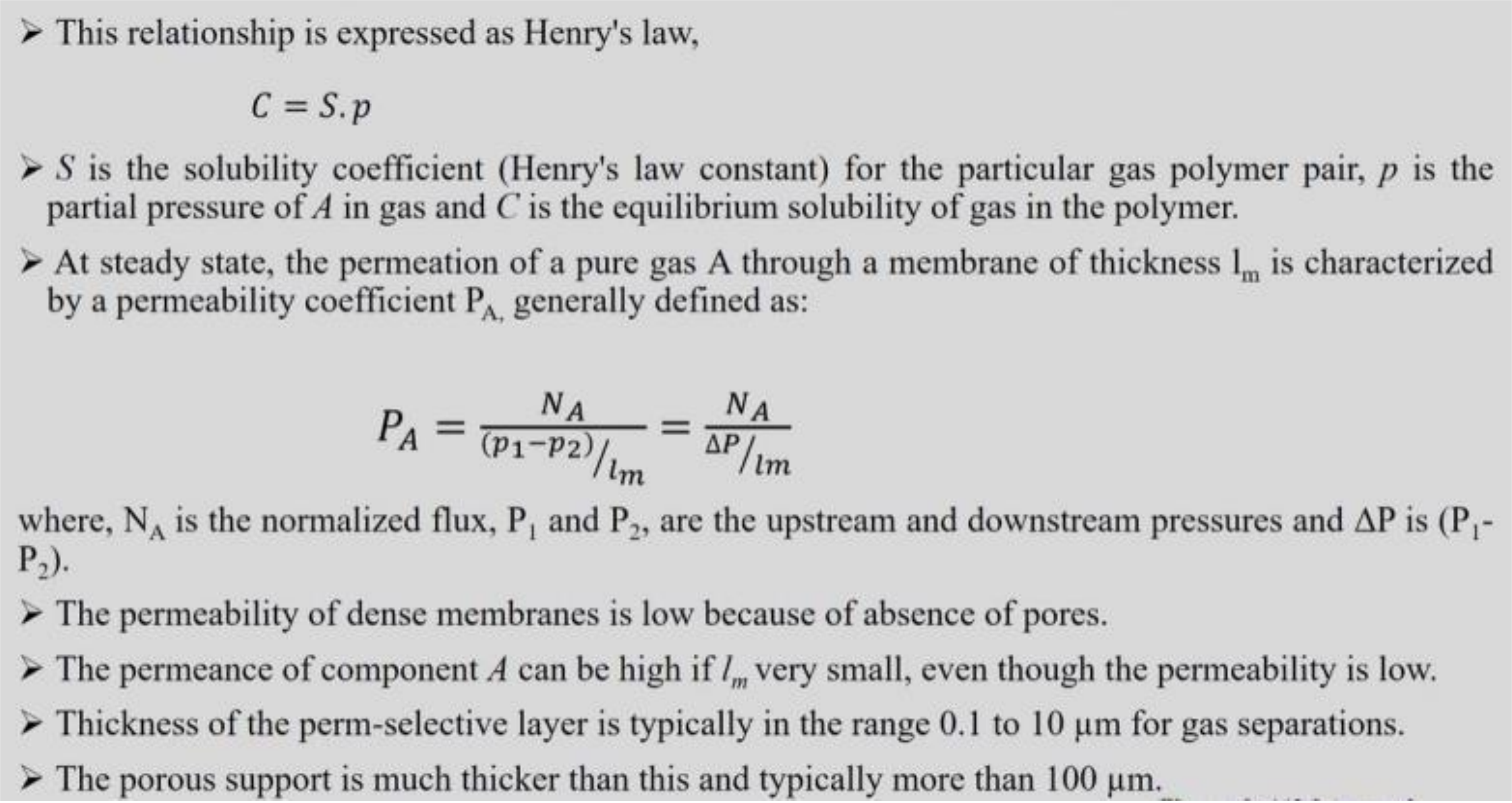
➢ Hence, it is the rate determining step in permeation.

➢ In general, the relationship between the linear flux J and the driving force is:

$$J = -D\frac{dc}{dx}, \text{ where } D \text{ is diffusion coefficient.}$$

➢ When the solubility of a penetrant gas in a polymer is sufficiently low, the concentration of the penetrant is proportional to the vapor pressure of penetrant in polymer.

Solution-Diffusion



- This relationship is expressed as Henry's law,

$$C = S.p$$

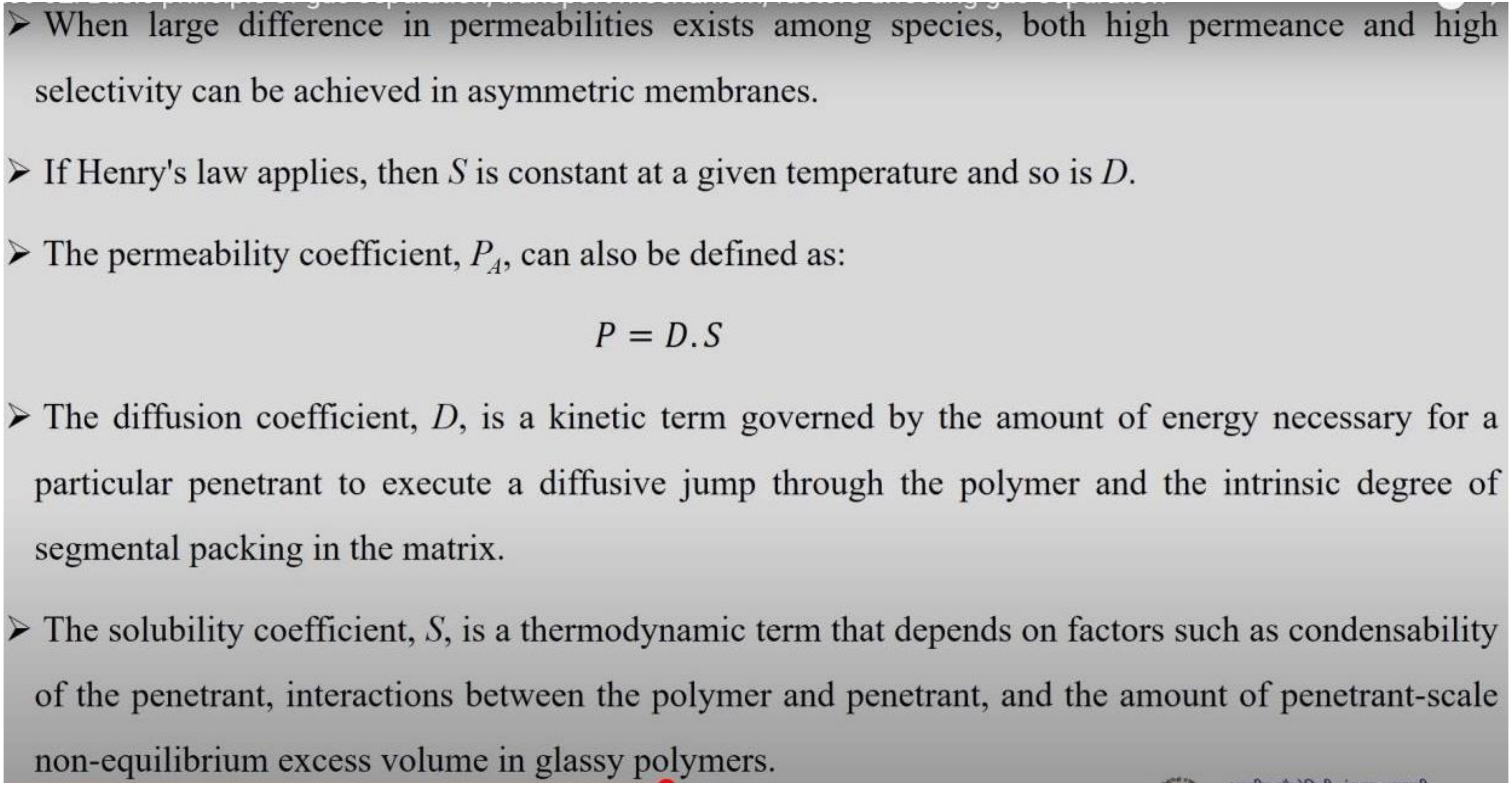
- S is the solubility coefficient (Henry's law constant) for the particular gas polymer pair, p is the partial pressure of A in gas and C is the equilibrium solubility of gas in the polymer.
- At steady state, the permeation of a pure gas A through a membrane of thickness l_m is characterized by a permeability coefficient $P_{A,}$ generally defined as:

$$P_A = \frac{N_A}{(p_1-p_2)/l_m} = \frac{N_A}{\Delta P/l_m}$$

where, N_A is the normalized flux, P_1 and P_2, are the upstream and downstream pressures and ΔP is (P_1-P_2).

- The permeability of dense membranes is low because of absence of pores.
- The permeance of component A can be high if l_m very small, even though the permeability is low.
- Thickness of the perm-selective layer is typically in the range 0.1 to 10 µm for gas separations.
- The porous support is much thicker than this and typically more than 100 µm.

Solution-Diffusion



- When large difference in permeabilities exists among species, both high permeance and high selectivity can be achieved in asymmetric membranes.
- If Henry's law applies, then S is constant at a given temperature and so is D.
- The permeability coefficient, P_A, can also be defined as:

$$P = D.S$$

- The diffusion coefficient, D, is a kinetic term governed by the amount of energy necessary for a particular penetrant to execute a diffusive jump through the polymer and the intrinsic degree of segmental packing in the matrix.
- The solubility coefficient, S, is a thermodynamic term that depends on factors such as condensability of the penetrant, interactions between the polymer and penetrant, and the amount of penetrant-scale non-equilibrium excess volume in glassy polymers.

Solution-Diffusion

The ability of a membrane to separate two molecules, *A* to *B*, is the ratio of their permeability, called as the membrane selectivity α.

$$\alpha = \frac{P_A}{P_B}$$

For a binary gas mixture the selectivity can also be determined from a molar concentration of the two gases in feed and permeate:

$$\alpha = \frac{y(1-x)}{x(1-y)}$$

where *y* is the permeate concentration of the fast permeating gas and *x* is its feed concentration.

- Expanding the permeability into diffusivity and solubility terms, the ideal selectivity can be expressed by,

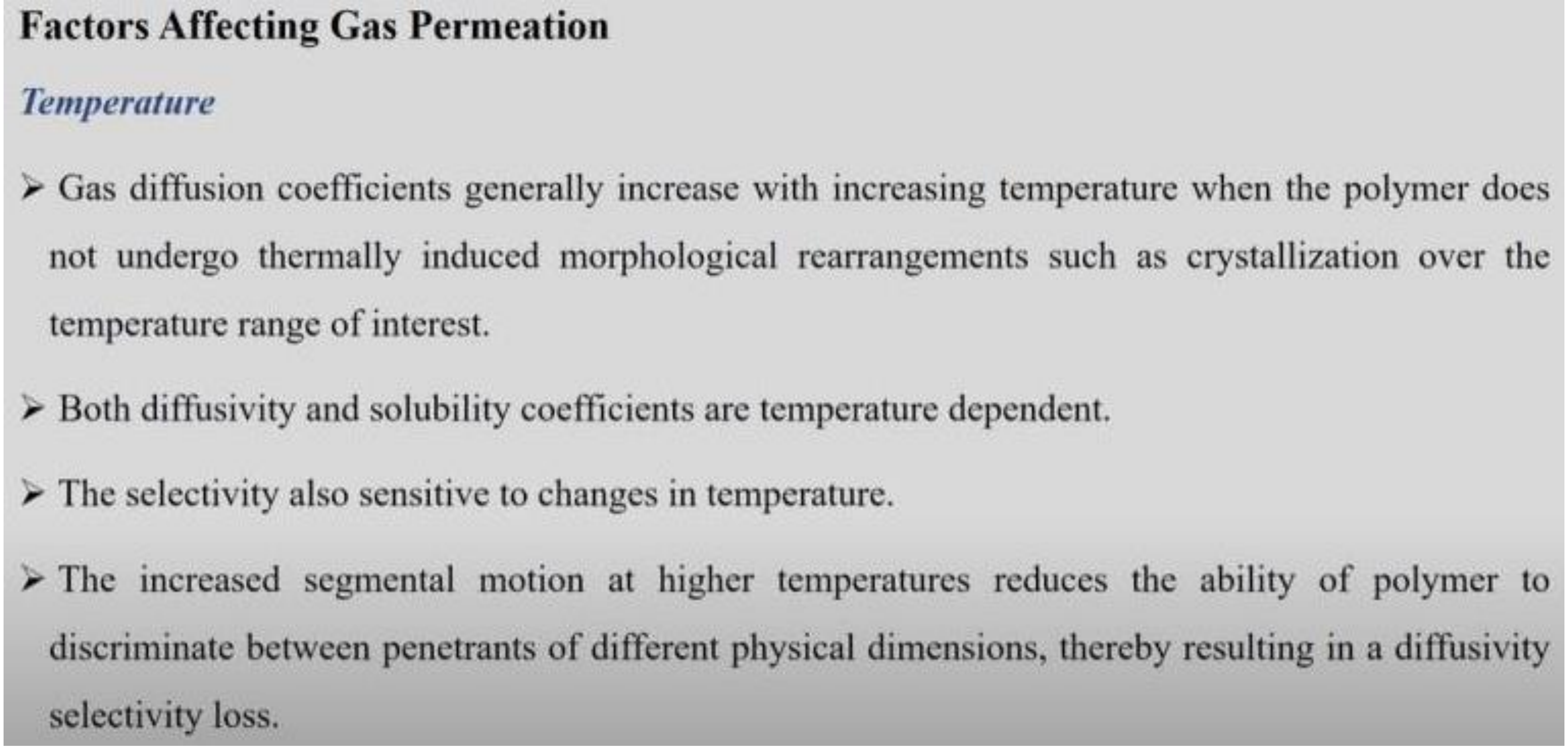
$$\boldsymbol{\alpha}_{\mathrm{AB}} = \left(\frac{D_A}{D_B}\right)\left(\frac{S_A}{S_B}\right)$$

Here, $\frac{D_A}{D_B}$ is the ratio of the concentration-averaged diffusion coefficients of penetrants *A* and *B* and referred to as the membranes diffusivity and $\frac{S_A}{S_B}$ is the ration of solubility selectivity.

The GS properties of membranes depend upon:

- the material (permeability, separation factors),
- the membrane structure and thickness (permeance),
- the membrane configuration (e.g., flat, hollow fiber) and
- the module and system design.

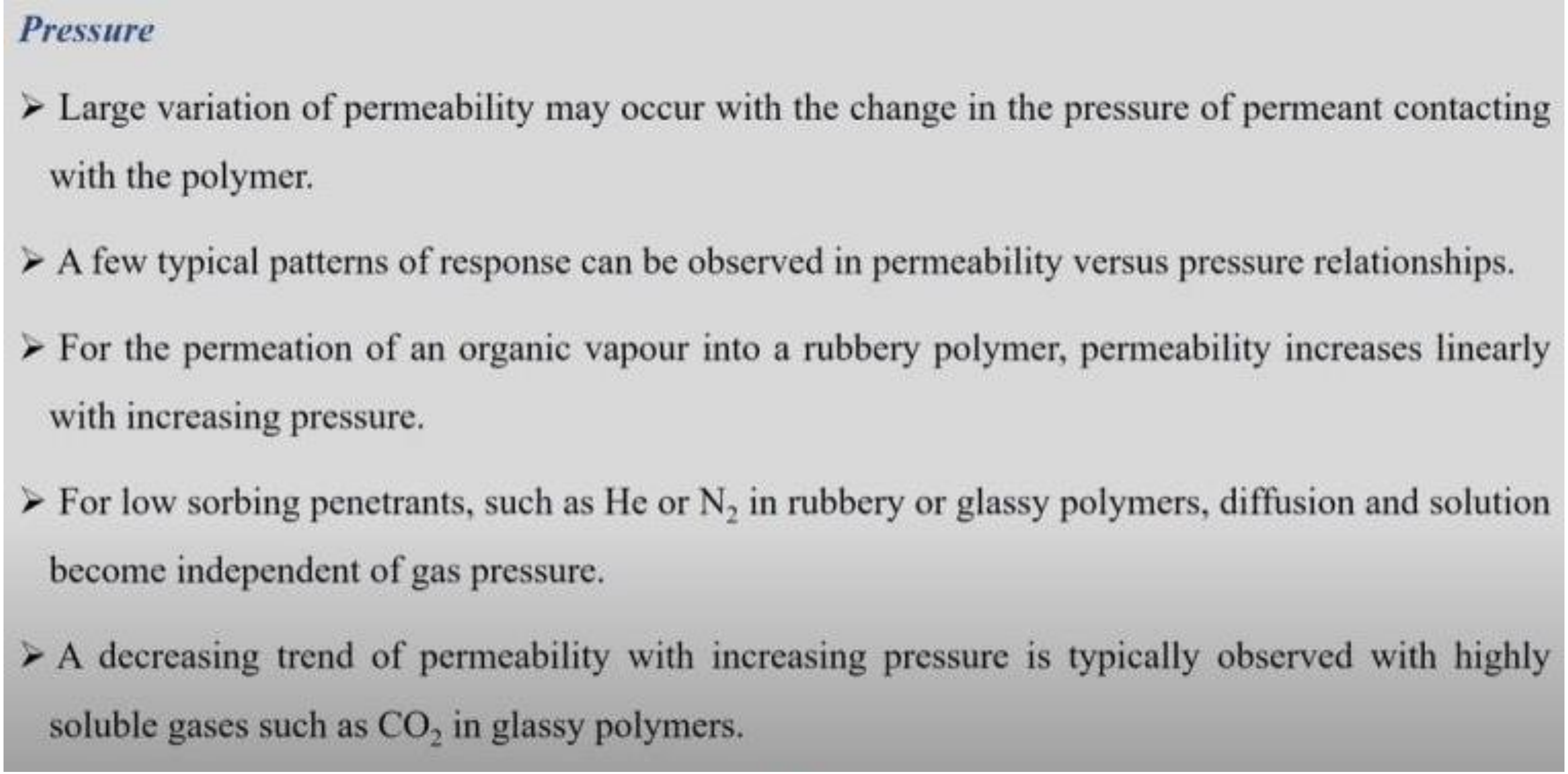
Both membrane's permeability and selectivity influence the economics of a GS membrane process.



Factors Affecting Gas Permeation

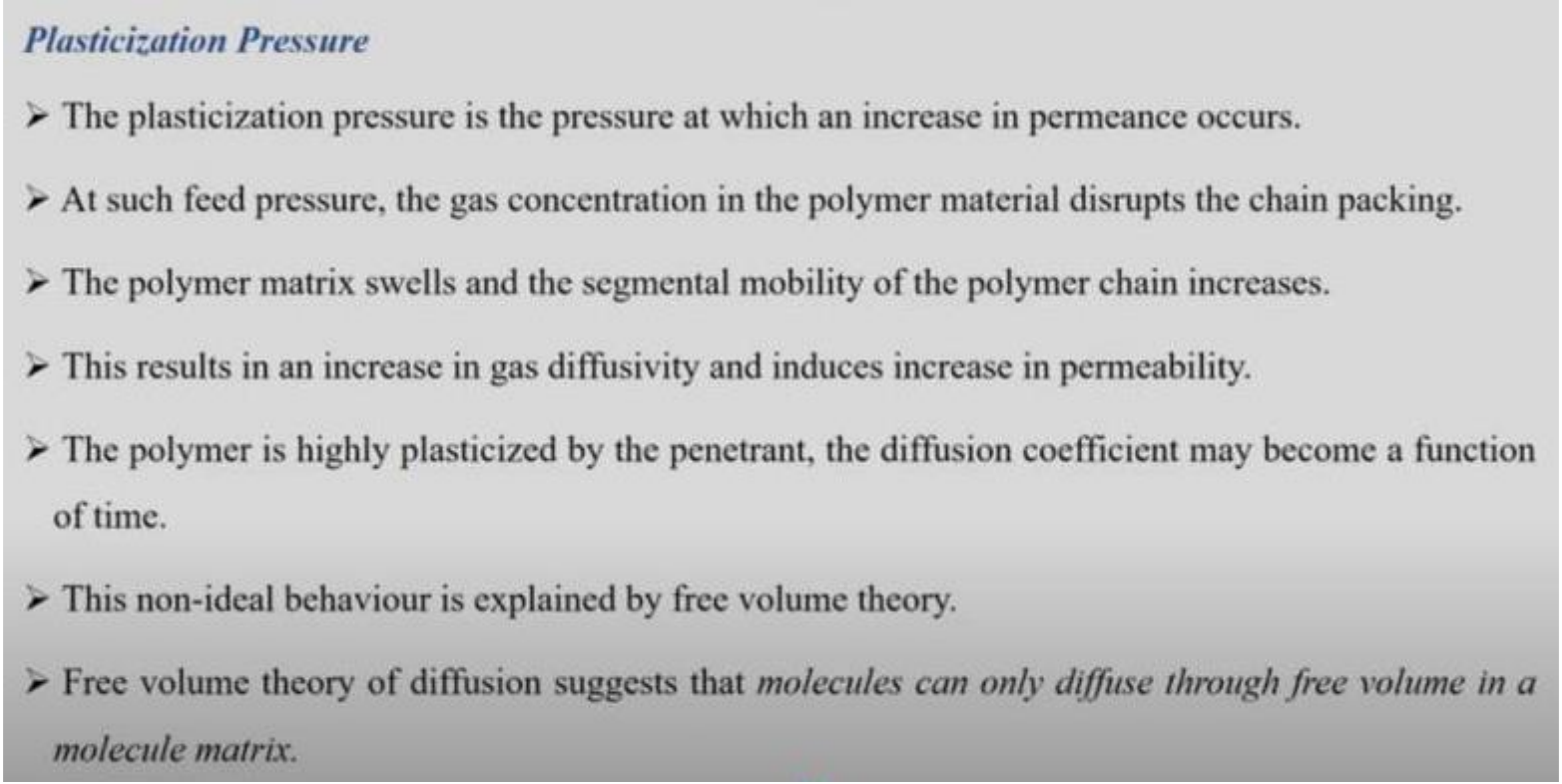
Temperature

- Gas diffusion coefficients generally increase with increasing temperature when the polymer does not undergo thermally induced morphological rearrangements such as crystallization over the temperature range of interest.
- Both diffusivity and solubility coefficients are temperature dependent.
- The selectivity also sensitive to changes in temperature.
- The increased segmental motion at higher temperatures reduces the ability of polymer to discriminate between penetrants of different physical dimensions, thereby resulting in a diffusivity selectivity loss.



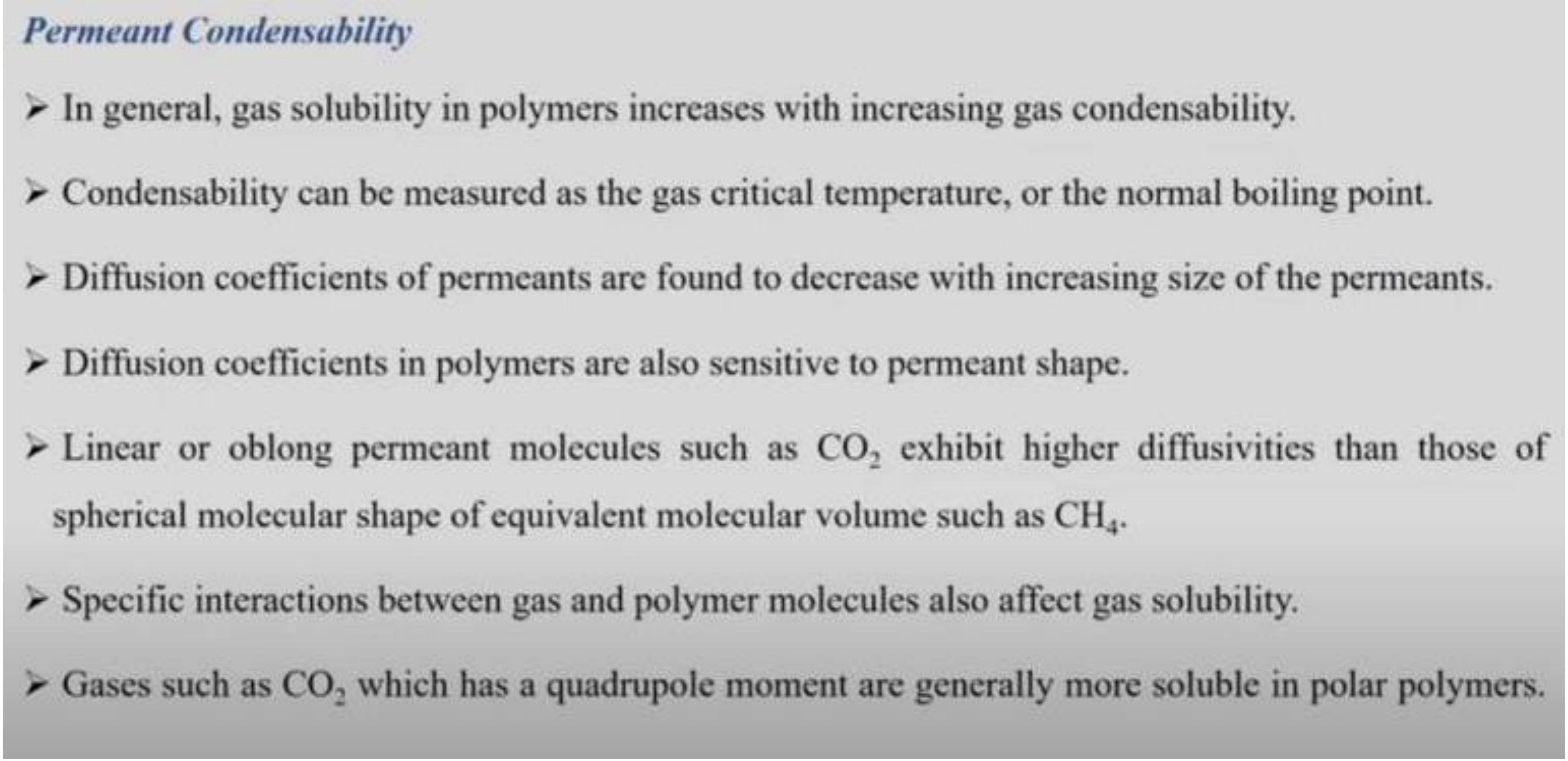
Pressure

- Large variation of permeability may occur with the change in the pressure of permeant contacting with the polymer.
- A few typical patterns of response can be observed in permeability versus pressure relationships.
- For the permeation of an organic vapour into a rubbery polymer, permeability increases linearly with increasing pressure.
- For low sorbing penetrants, such as He or N_2 in rubbery or glassy polymers, diffusion and solution become independent of gas pressure.
- A decreasing trend of permeability with increasing pressure is typically observed with highly soluble gases such as CO_2 in glassy polymers.



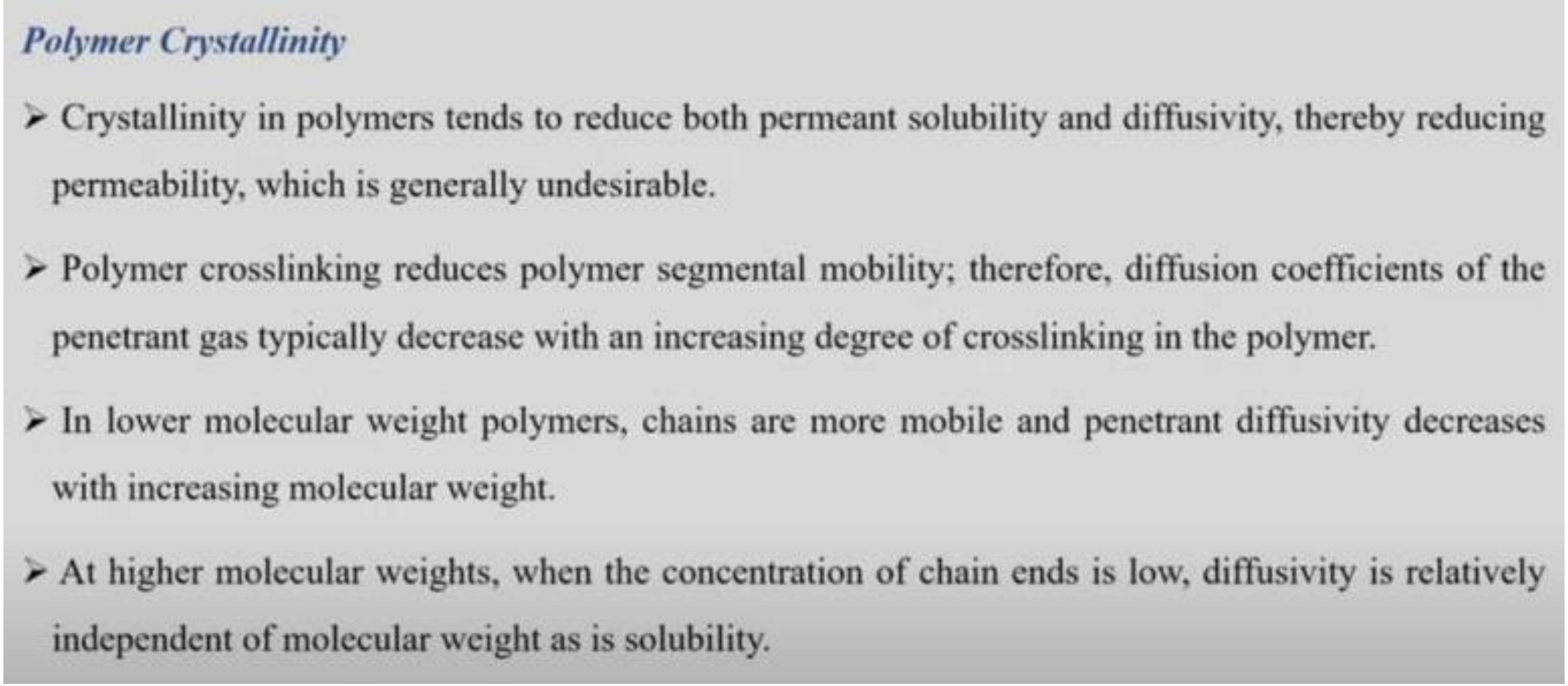
Plasticization Pressure

- The plasticization pressure is the pressure at which an increase in permeance occurs.
- At such feed pressure, the gas concentration in the polymer material disrupts the chain packing.
- The polymer matrix swells and the segmental mobility of the polymer chain increases.
- This results in an increase in gas diffusivity and induces increase in permeability.
- The polymer is highly plasticized by the penetrant, the diffusion coefficient may become a function of time.
- This non-ideal behaviour is explained by free volume theory.
- Free volume theory of diffusion suggests that *molecules can only diffuse through free volume in a molecule matrix.*



Permeant Condensability

- In general, gas solubility in polymers increases with increasing gas condensability.
- Condensability can be measured as the gas critical temperature, or the normal boiling point.
- Diffusion coefficients of permeants are found to decrease with increasing size of the permeants.
- Diffusion coefficients in polymers are also sensitive to permeant shape.
- Linear or oblong permeant molecules such as CO_2 exhibit higher diffusivities than those of spherical molecular shape of equivalent molecular volume such as CH_4.
- Specific interactions between gas and polymer molecules also affect gas solubility.
- Gases such as CO_2 which has a quadrupole moment are generally more soluble in polar polymers.



Polymer Crystallinity

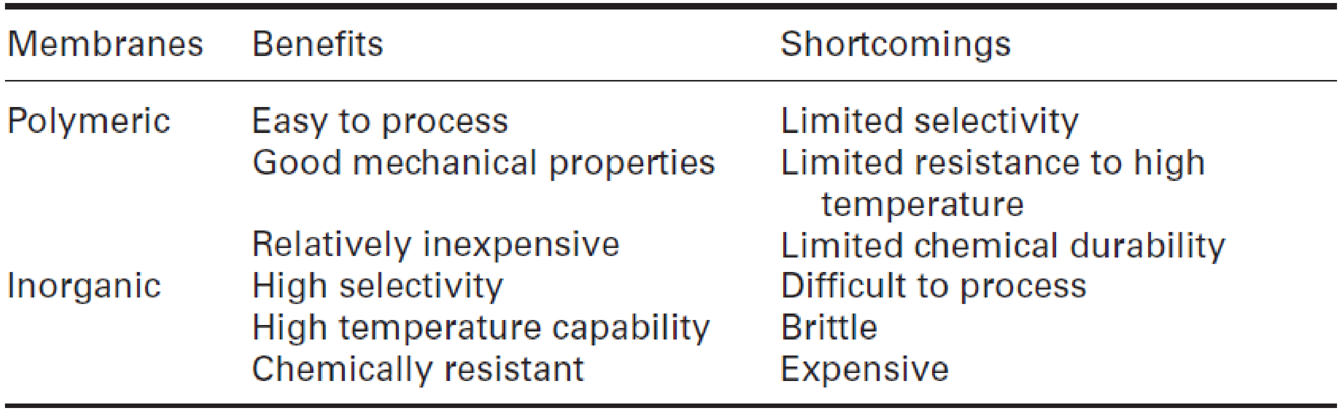
- Crystallinity in polymers tends to reduce both permeant solubility and diffusivity, thereby reducing permeability, which is generally undesirable.
- Polymer crosslinking reduces polymer segmental mobility; therefore, diffusion coefficients of the penetrant gas typically decrease with an increasing degree of crosslinking in the polymer.
- In lower molecular weight polymers, chains are more mobile and penetrant diffusivity decreases with increasing molecular weight.
- At higher molecular weights, when the concentration of chain ends is low, diffusivity is relatively independent of molecular weight as is solubility.

Membrane for Gas Separation

- The majority of industrial membrane processes for gas separations utilize glassy polymeric membranes because of their high gas selectivity and good mechanical properties.
- Glassy polymers like polyimides are used for CO_2/CH_4 separation; polysulfones are used in H_2 separations; and cellulose acetate membranes are used for the removal of CO_2 and H_2O from natural gas.
- In the area of rubbery polymers, polyurethanes possess high permeability and are being applied in O_2/N_2 separation.

TYPES OF MEMBRANE MATERIALS

- Inorganic
- Polymeric/Organic
- Mixed Matrix Membrane
  - Inorganic fillers integrated into the polymer matrix
  - Higher permeability and selectivity



Membranes	Benefits	Shortcomings
Polymeric	Easy to process Good mechanical properties Relatively inexpensive	Limited selectivity Limited resistance to high temperature Limited chemical durability
Inorganic	High selectivity High temperature capability Chemically resistant	Difficult to process Brittle Expensive

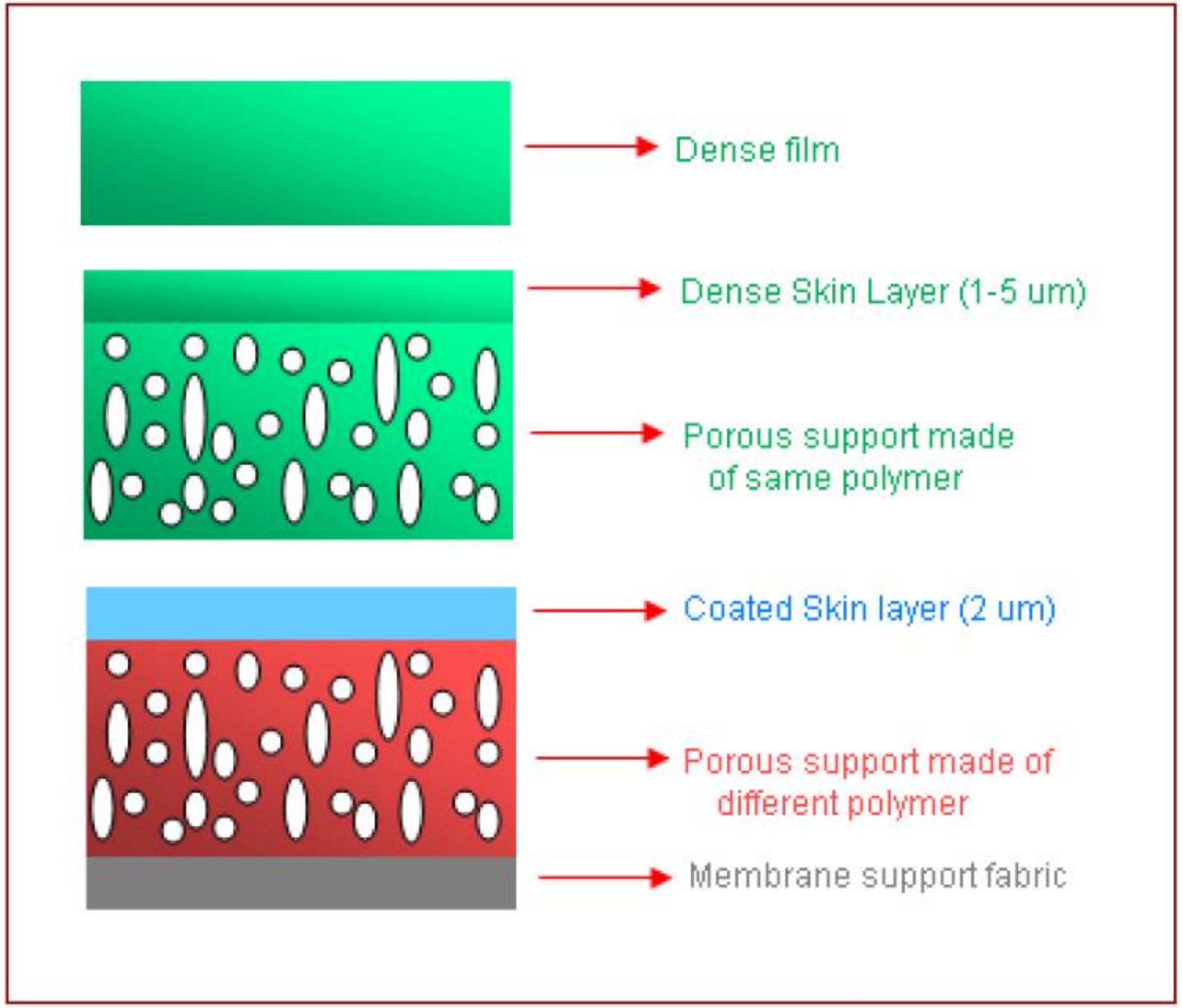


Fig. 7. Schematic Representation of Three Different Types of Membrane Morphologies (a) Homogeneous Symmetric (b) Asymmetric Membrane and (c) TFC Membrane

UPSCALING OF GAS MEMBRANE

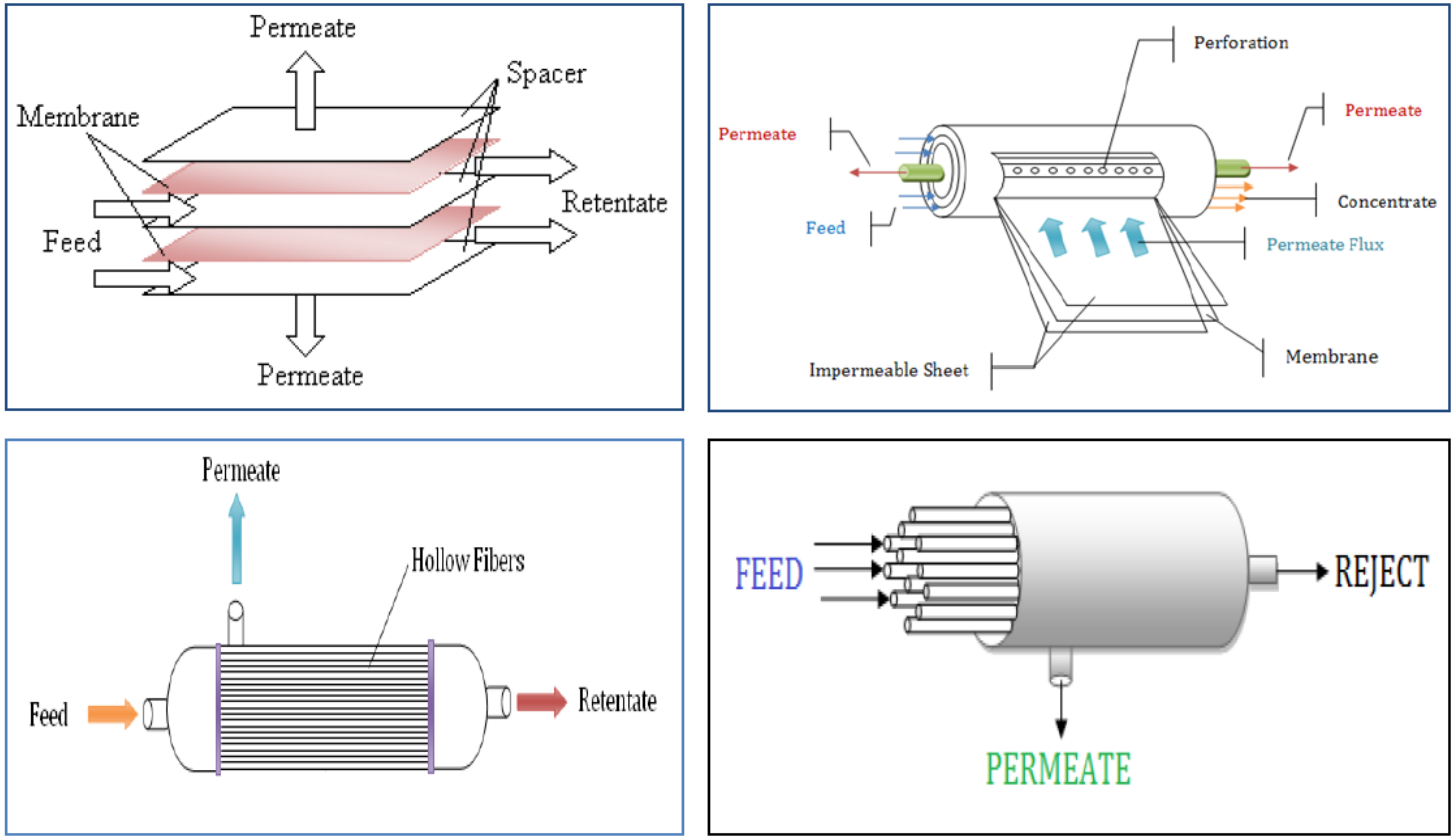


Fig. 12. Schematic Diagrams of (a) Plate and Frame Module, (b) Spiral-wound, (c) Hollow fiber and (d) Tubular Membrane Module Configurations

Table 2. Predicted Sales of Membrane Gas Separation in Main Target Markets

Type of Separation	**Membrane Market (US$ Million)**	
	2010	**2020**
Isolation of Inert N_2 from Air	100	125
O_2 Enrichment from Air	10	30
H_2 Recovery	60	150
CO_2 Removal from Natural Gas	60	100
Vapor/Nitrogen Separation	30	60
Vapor/Vapor Separation	20	100
Removal of Moisture from Air and others	30	100

Table 3. Major Global Suppliers of Gas Membrane Systems

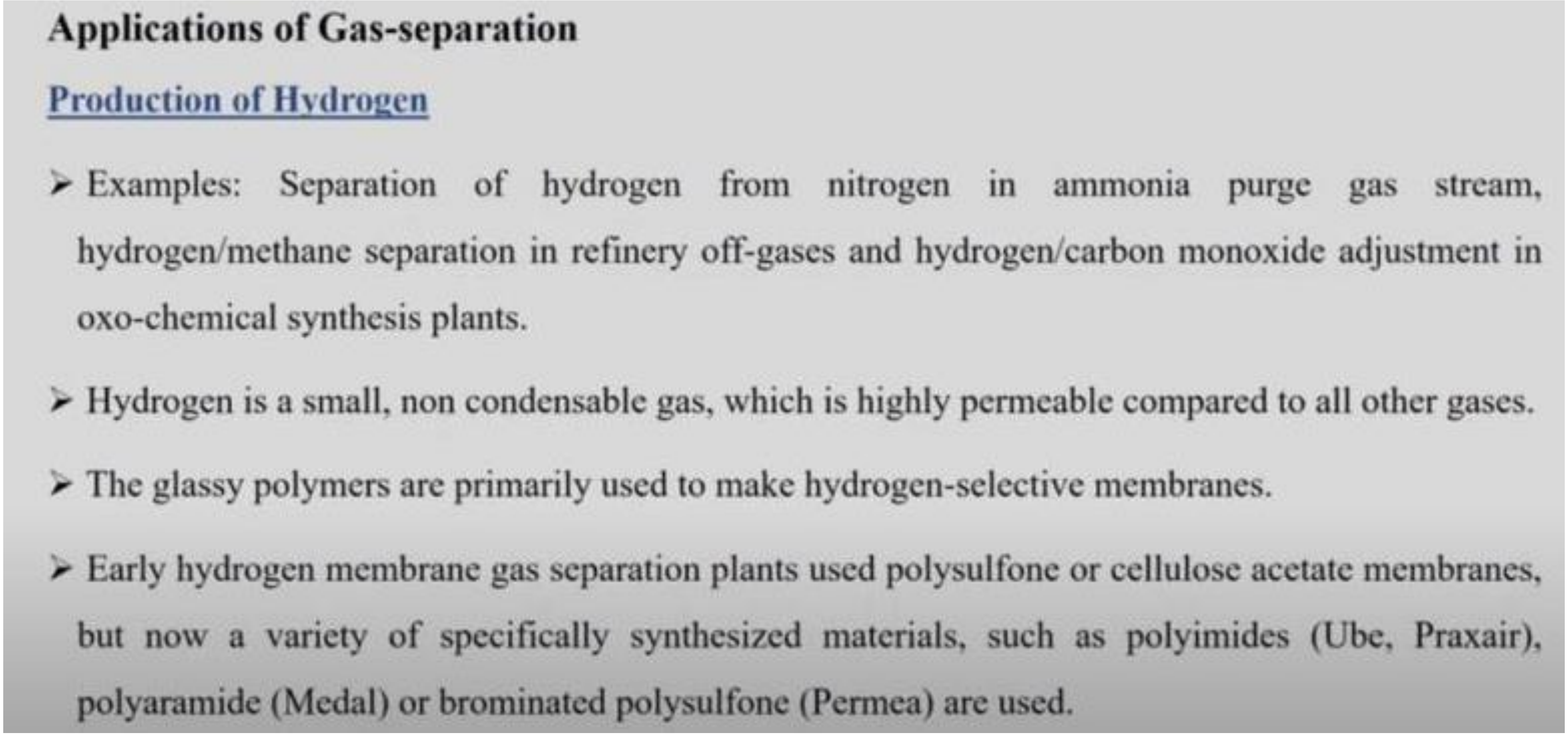
Gas Mixture	Application	Supplier	Country
O_2/N_2	Nitrogen generation Oxygen enrichment	Perma (Air Products), Generon (IGS), IMS (Praxair), Medal (Air Liquide), Parker Gas Separation, Ube	USA USA Canada USA USA USA
H_2/Hydrocarbons	Refinery H_2 recovery	Air Products, Air Liquide, Ube, Praxair	USA Canada
H_2/CO	Syngas ratio adjustment	Air Products, Air Liquide, Ube, Praxair	USA Canada
H_2/N_2	Recovery of H_2 from ammonia purge gas	Air Products, Air Liquide, Ube, Praxair	USA Canada
CO_2/CH_4	Acid gas treatment, Enhanced oil recovery, Upgrading landfill gas	Cynara (NATCO) Air Products, Ube, Kvaerner	USA USA Norway
H_2S/ Hydrocarbons	Sour gas treatment	Cynara (NATCO) Air Products, Ube, Kvaerner	USA USA Norway
H_2O/ Hydrocarbons	Natural gas dehydration	Kvaerner, Air Products.	Norway USA
H_2O/Air	Air dehydration	Air Products, Parker Balson, Praxair	USA Canada
Hydrocarbons/Air	Pollution control, Hydrocarbon recovery	Borsig, GMT, MTR	Germany Canada

Table 4. List of Commercial Gas Membranes and their Modular Configurations

Polymer	Module type	Gas Mixture System	Manufacturer
Polysulfone	Hollow fiber	O_2, N_2, H_2, H_2O, CO_2	Perma (Air products)
Polyimide/polyaramide	Hollow fiber	H_2,N_2,O_2	Medal (Air Liquide)
Tetrabromo polycarbonate	Hollow fiber	N_2	Generon (MG Industries)
Polyimide	Hollow fiber	N_2, H_2O	IMS (Praxair)
Cellulose acetate	Spiral wound	CO_2 CO_2, H_2	Kvaerner Separex (UOP)
Cellulose acetate	Hollow fiber	CO_2	Cynara (Dow)
Polyimide	Hollow fiber	Air dehydration	Perker Hannifin
Polyimide	Hollow fiber	O_2, N_2, H_2	Ube
Silicone rubber	Plate and frame	VOCs	GKSS licensees
Silicone rubber	Spiral wound	VOCs	MTR

Table 7. Main Industrial Applications of Membrane GS

separation	process
H_2/N_2	ammonia purge gas
H_2/CO	syngas ratio adjustment
H_2/hydrocarbons	hydrogen recovery in refineries
O_2/N_2	nitrogen generation, oxygen-enriched air production
CO_2/hydrocarbons (CH_4)	natural gas sweetening, landfill gas upgrading
H_2O/hydrocarbons (CH_4)	natural gas dehydration
H_2S/hydrocarbons	sour gas treating
He/hydrocarbons	helium separation
He/N_2	helium recovery
hydrocarbons/air	hydrocarbons recovery, pollution control
H_2O/air	air dehumidification
volatile organic species (e.g., ethylene or propylene)/ light gases (e.g., nitrogen)	polyolefin purge gas purification



Applications of Gas-separation

Production of Hydrogen

- Examples: Separation of hydrogen from nitrogen in ammonia purge gas stream, hydrogen/methane separation in refinery off-gases and hydrogen/carbon monoxide adjustment in oxo-chemical synthesis plants.
- Hydrogen is a small, non condensable gas, which is highly permeable compared to all other gases.
- The glassy polymers are primarily used to make hydrogen-selective membranes.
- Early hydrogen membrane gas separation plants used polysulfone or cellulose acetate membranes, but now a variety of specifically synthesized materials, such as polyimides (Ube, Praxair), polyaramide (Medal) or brominated polysulfone (Permea) are used.

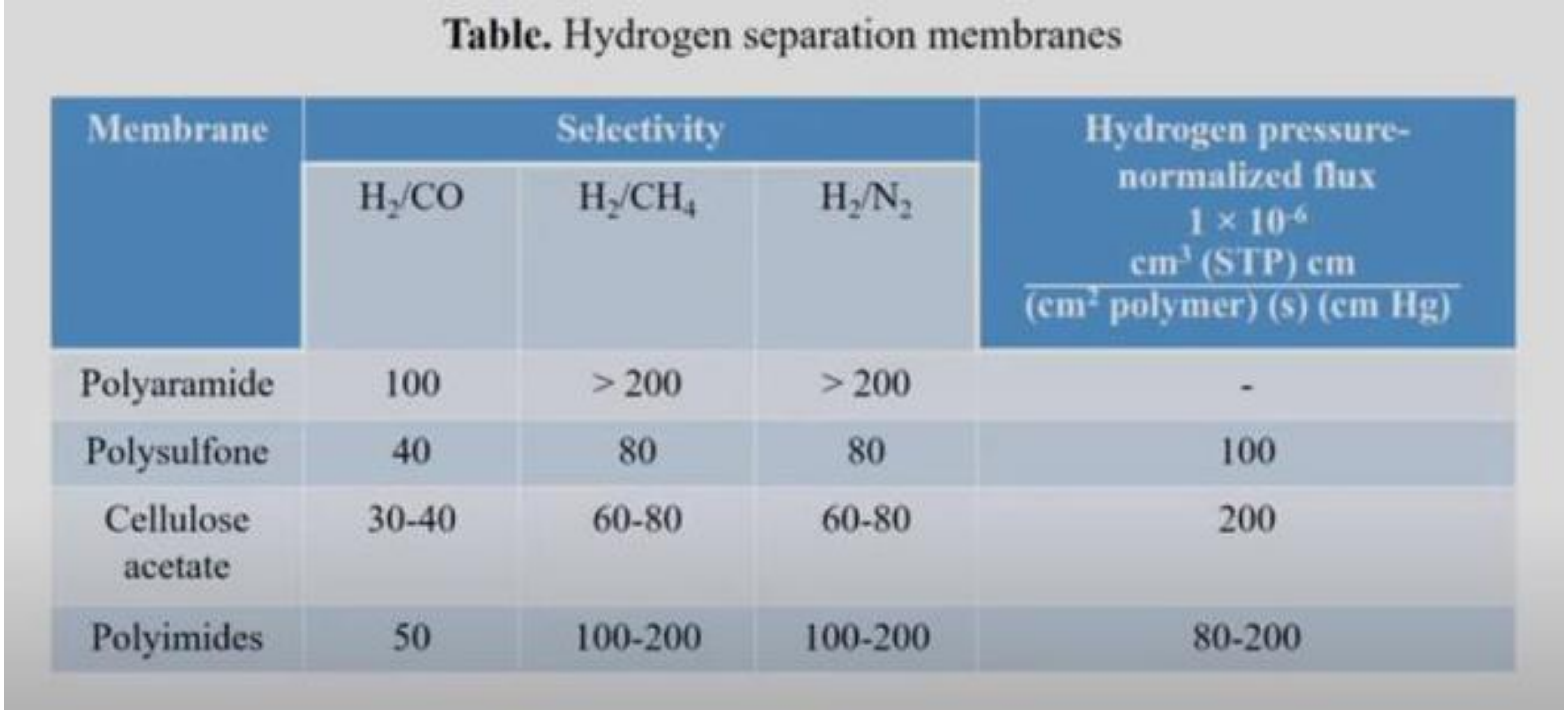
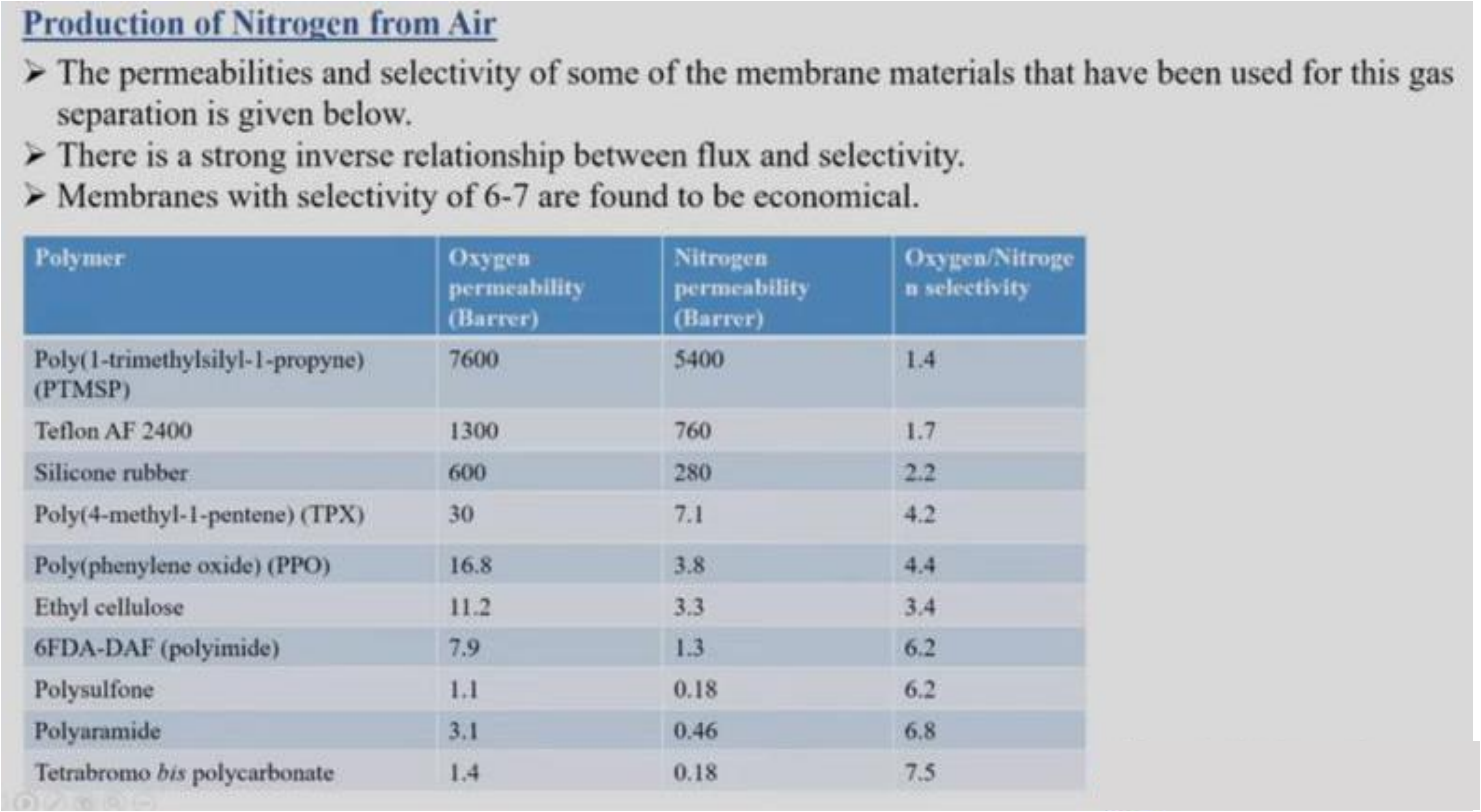


Table. Hydrogen separation membranes

Membrane	**Selectivity**			**Hydrogen pressure-normalized flux** $1 \times 10^{-6} \frac{cm^3\,(STP)\,cm}{(cm^2\ polymer)\,(s)\,(cm\ Hg)}$
	H_2/CO	H_2/CH_4	H_2/N_2	
Polyaramide	100	> 200	> 200	-
Polysulfone	40	80	80	100
Cellulose acetate	30-40	60-80	60-80	200
Polyimides	50	100-200	100-200	80-200



Production of Nitrogen from Air

- The permeabilities and selectivity of some of the membrane materials that have been used for this gas separation is given below.
- There is a strong inverse relationship between flux and selectivity.
- Membranes with selectivity of 6-7 are found to be economical.

Polymer	Oxygen permeability (Barrer)	Nitrogen permeability (Barrer)	Oxygen/Nitrogen selectivity
Poly(1-trimethylsilyl-1-propyne) (PTMSP)	7600	5400	1.4
Teflon AF 2400	1300	760	1.7
Silicone rubber	600	280	2.2
Poly(4-methyl-1-pentene) (TPX)	30	7.1	4.2
Poly(phenylene oxide) (PPO)	16.8	3.8	4.4
Ethyl cellulose	11.2	3.3	3.4
6FDA-DAF (polyimide)	7.9	1.3	6.2
Polysulfone	1.1	0.18	6.2
Polyaramide	3.1	0.46	6.8
Tetrabromo *bis* polycarbonate	1.4	0.18	7.5

- This selectivity/permeability trade-off is very apparent in the plot of selectivity as a function of oxygen permeability.

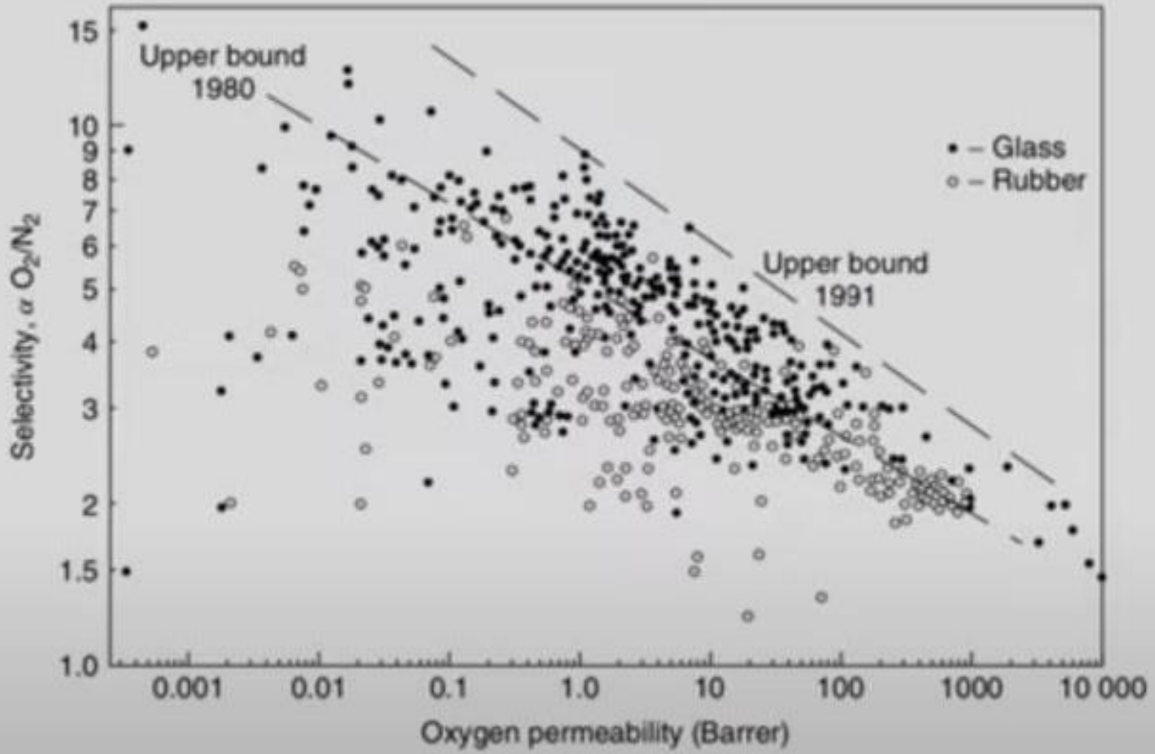
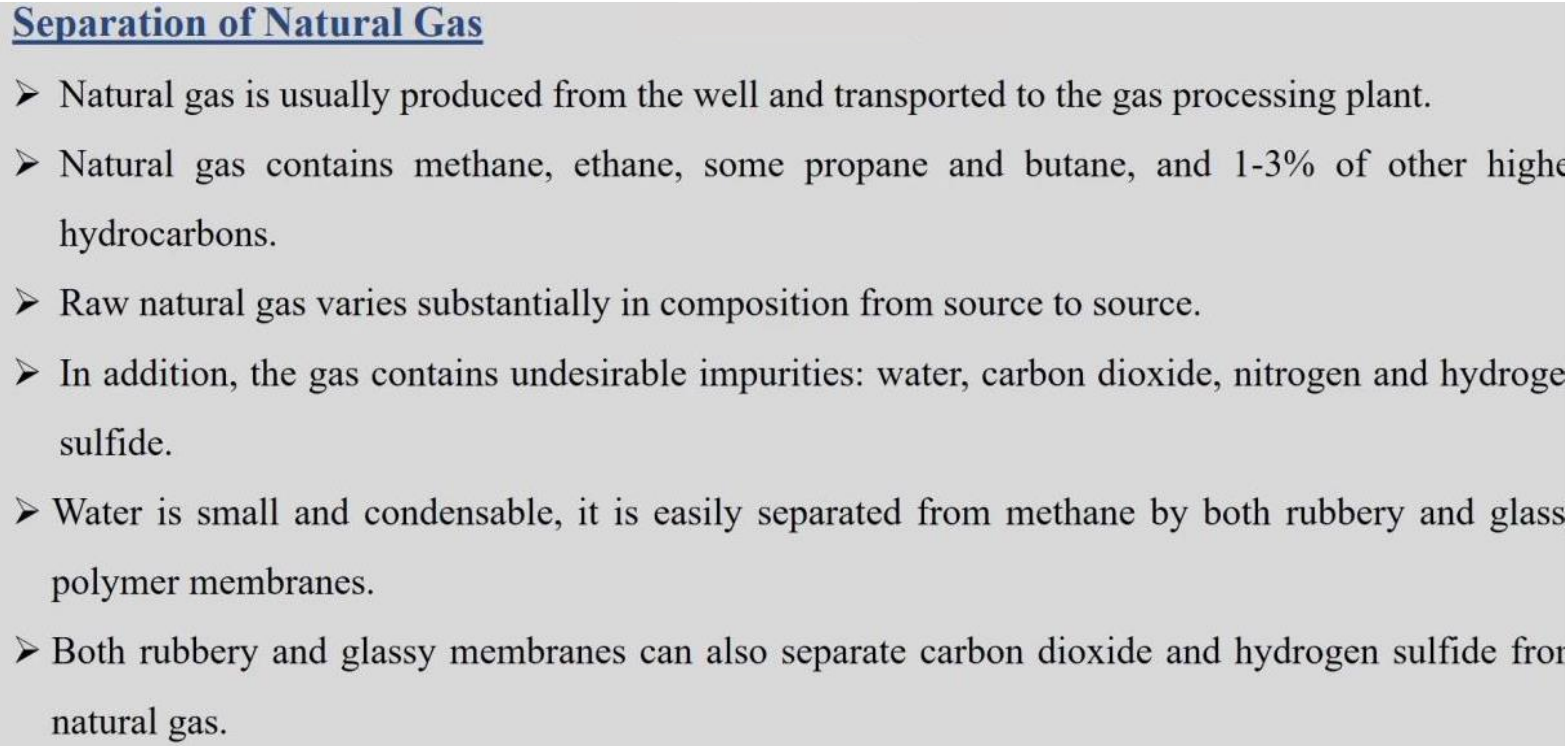
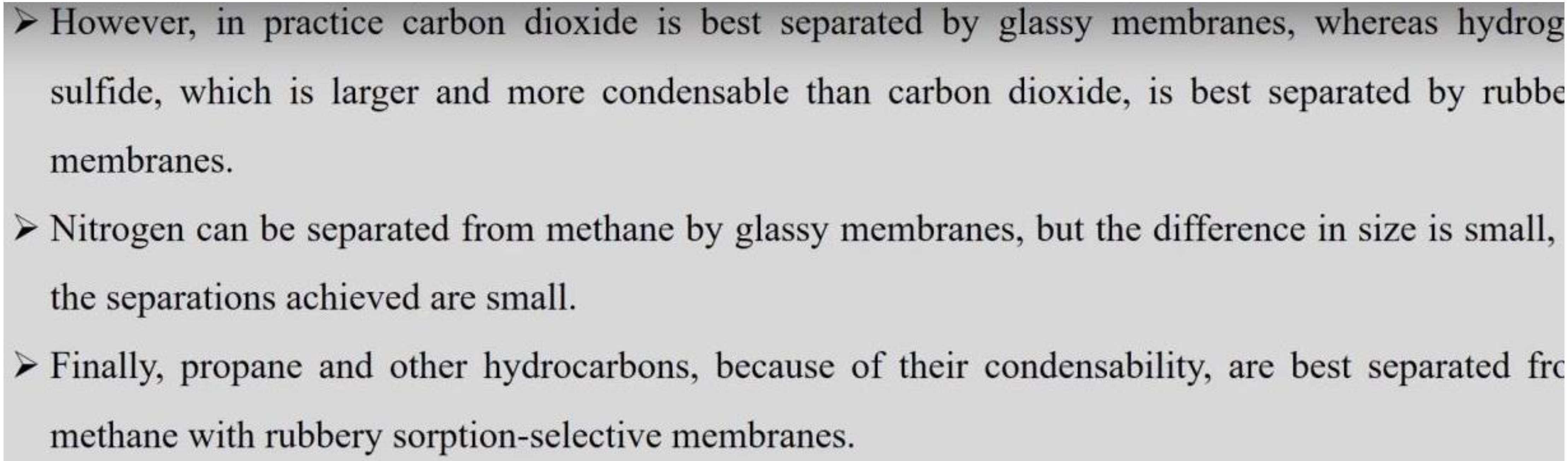


Figure. Oxygen/nitrogen selectivity as a function of oxygen permeability



Separation of Natural Gas

- Natural gas is usually produced from the well and transported to the gas processing plant.
- Natural gas contains methane, ethane, some propane and butane, and 1-3% of other highe hydrocarbons.
- Raw natural gas varies substantially in composition from source to source.
- In addition, the gas contains undesirable impurities: water, carbon dioxide, nitrogen and hydroge sulfide.
- Water is small and condensable, it is easily separated from methane by both rubbery and glass polymer membranes.
- Both rubbery and glassy membranes can also separate carbon dioxide and hydrogen sulfide fror natural gas.



- However, in practice carbon dioxide is best separated by glassy membranes, whereas hydrog sulfide, which is larger and more condensable than carbon dioxide, is best separated by rubbe membranes.
- Nitrogen can be separated from methane by glassy membranes, but the difference in size is small, the separations achieved are small.
- Finally, propane and other hydrocarbons, because of their condensability, are best separated frc methane with rubbery sorption-selective membranes.

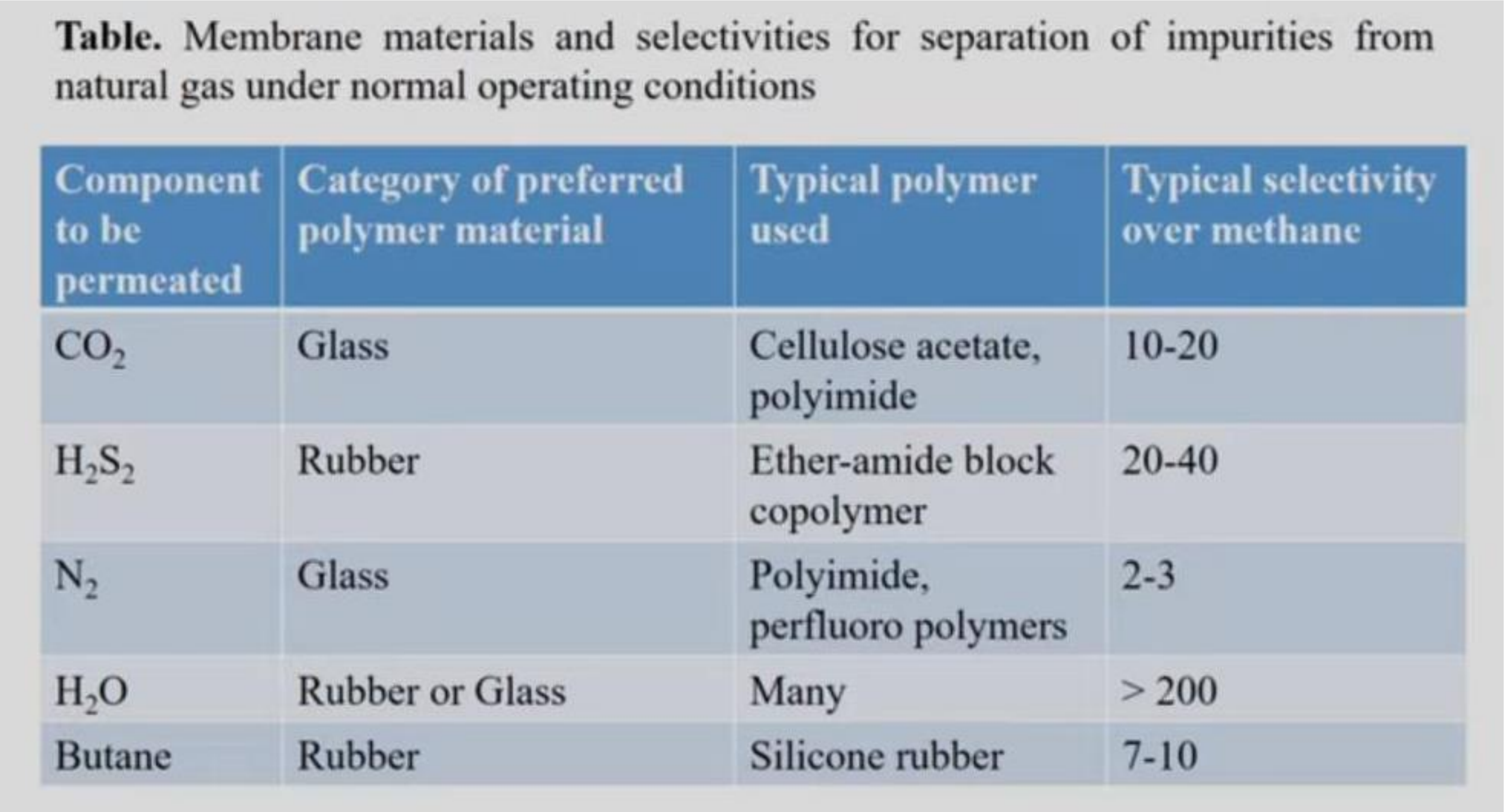


Table. Membrane materials and selectivities for separation of impurities from natural gas under normal operating conditions

Component to be permeated	Category of preferred polymer material	Typical polymer used	Typical selectivity over methane
CO_2	Glass	Cellulose acetate, polyimide	10-20
H_2S_2	Rubber	Ether-amide block copolymer	20-40
N_2	Glass	Polyimide, perfluoro polymers	2-3
H_2O	Rubber or Glass	Many	> 200
Butane	Rubber	Silicone rubber	7-10