Membrane Separation Processes

Many processes for separation of gases or liquid mixtures use semipermeable membranes that allow one or more constituents of the mixture to pass through more readily than the others. The membranes may be thin layers of a rigid materials such as porous glass or sintered metal, but more often they are flexible films of synthetic polymers prepared to have a high permeability for certain types of molecules.

Separation of gases:-

Porous membranes:- When a gas mixture is allowed to diffuse through a porous membrane to a region of lower pressure, the gas permeating the membrane is enriched in the lower molecular weight components, since they diffuse more rapidly. When the pore are much smaller than the mean free path in the gas phase, the gas diffuse independently by Knudsen diffusion, and the diffusivity in the pore is proportion to the pore size.

$$\underset{cm^2/s}{D_A} = 9700 \underset{(cm)}{r} \sqrt{\frac{T}{M}}$$ (for cylindrical pores)

(Based on total membrane area) $$D_{eA} = \frac{D_A \varepsilon}{\tau} = \frac{1}{4} D_A$$ $\frac{\varepsilon}{\tau}$ (0.2 to 0.3) if $\varepsilon = 0.5$

τ tortuosity, ε Porosity

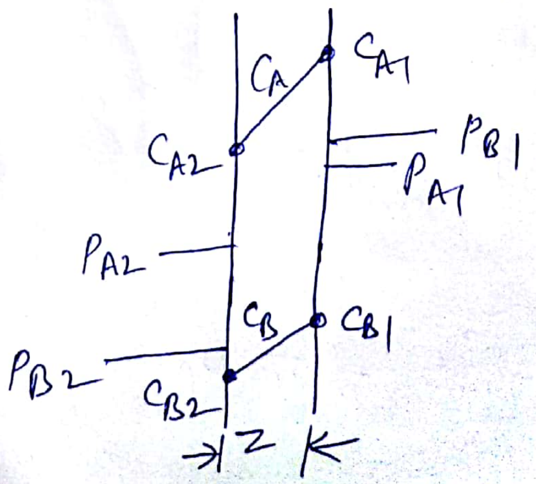
Flux of each gas is given as

$$J_A = D_{eA}\left(\frac{\Delta C_A}{\Delta z}\right) = D_{eA}\left(\frac{\Delta P_A/RT}{\Delta z}\right)$$

The composition of permeate depends on the fluxes of all species, for a binary system, the mole fraction of A in the permeate is

$$y_A = \frac{J_A}{J_A + J_B}$$

Polymer membranes:- The transport of gases through dense (nonporous) polymer membranes occurs by a solution - diffusion mechanism. The gas dissolves in the polymer at the high-pressure side of the membranes, diffuses through the polymer phase, and desorbs or evaporates at the low-pressure side. The rate of mass transfer depends on the conc. gradient in the membrane, which is proportional to the pressure gradient across the membran if the solubility is proportion to the pressure.



The flux for gas A is

$$J_A = -D_A\left(\frac{dC_A}{dz}\right) = D_A\left(\frac{C_{A1}-C_{A2}}{z}\right)$$

$C_A = P_A S_A$ $C_B = P_B S_B$

S = solubility coefficient (mole/cm^3-atm) (reciprocal to Henry's law coeff.)

$$J_A = \frac{D_A S_A (P_{A1}-P_{A2})}{z}$$

$D_A S_A$ is the flux per unit pressure gradient, which is called the permeability coefficient q_A and is often expressed in Barrers, where

1 Barrer = 10^{-10} cm^3(STP) -cm/ cm^2-s-cmHg

since actual membrane thickness is not always known or specified for commercial membranes, it is customary to use the flux per unit pressure difference, which will be called the permeability Q_A

$$J_A = \frac{q_A (P_{A1}-P_{A2})}{z} = Q_A (P_{A1}-P_{A2})$$

units of Q may be std ft^3/ft^2-h-atm

or L(STP)/m^2-h-atm

The ratio of permeabilities for a binary mixture is the membrane selectivity α (also called the ideal separation factor)

$$\alpha = \frac{Q_A}{Q_B} = \frac{D_A S_A}{D_B S_B}$$

A hight selectivity can be obtained from either a favorable diffusivity ratio or a large difference in solubilities.

diffusivity in membrane D_A depends more strongly on shape and size of molecules than ~~diffusion~~ gas phase diffusivity.

The gas solubility varies widely with the gas and type of polymer. The solubility is low for gases that have a low boiling point or critical temp., but similarity of gas and polymer is also important. polar gases tend to be more soluble in polymers with a high conc. of polar groups, and the solubility of water vapor is high in materials that can form hydrogen bonds with water molecules.

For most gases, permeability increases with temp.

~~because~~

$$Q = a \exp(-E/RT) \qquad E = 1-5 \text{ Kcal/mol}$$

However, an increase in temp usually decreases the membrane selectivity, so the operating temp. is determined by balancing the needs for flux and high selectivity

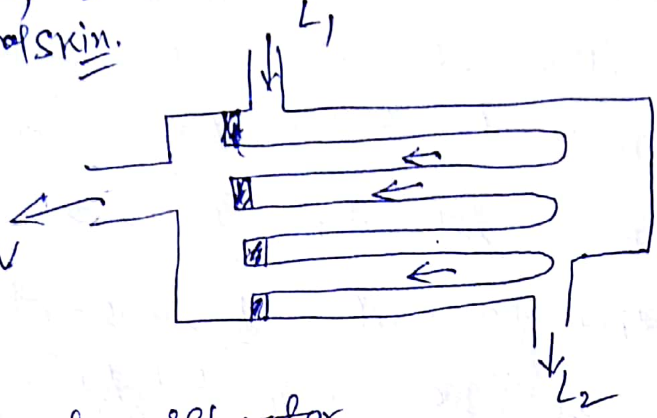
Membrane structure:- The flux through a dense ~~membrane~~ polymer film is inversely proportional to the thickness, so there is a strong incentive to make the membrane as thin as possible without having holes or weak spots in it. Gas separation processes operate with pressure differences of 1 to 20 atm, so thin membrane must be supported by a porous structure capable of withstanding such pressures but offering little resistance to the flow of gas. The support is made from a porous ceramic, metal or polymer and it should have a porosity of about 50%. The pore size should be comparable to the thickness of the thin selective film that covers the support. However handling a thin layer and bonding it to the support without tearing is difficult, and hence most gas separation membranes are prepared with the support as an integral part of the membrane.

Most gas separation membranes are 50 – 200 µm thick with a 0.1 – 1 µm skin. New techniques may permit production of commercial membranes with a skin thinner than 0.1 µm.

[The asymmetric membrane can be prepared in form of flat sheets, tube, or hollow fibers as small as 40 µm in diameter]

Flow patterns in membrane separators:-

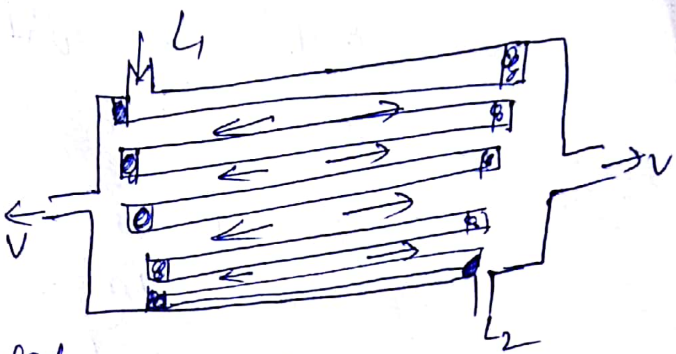
There are several ways of arranging the surface area in a gas separator, Below fig shows hollow fiber membrane with an external skin.



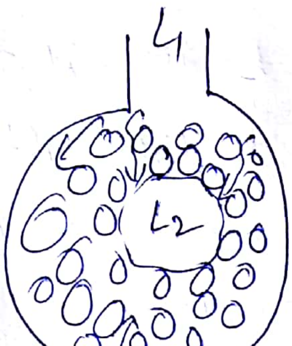
Counter current

A commerical seperator has upto million fibers in a shell several inches in diameter.

The fibers are sealed into a tube sheet with an epoxy potting compound at one or both ends of the unit to keep the feed and permeate separated.



Parallel and counter current



Radial crossflow

Fibers are bundled around a perforated discharge pipe, and the feed gas flows radially from the outside of the shell to the central pipe.

Some commercial separators are arranged with feed at the center and radial flow outward. The fibers can be sealed in tube sheets at one or both ends of the unit.

Scanned by CamScanner

Product purity and yield

The composition of the permeate and the residue depend on the pressure difference across the membrane, the permeability of various species, the feed composition, and the fraction of the feed that is recovered as permeate.

The fluxes are given by the following equations where P_1 is the feed pressure and P_2 the permeate pressure.

For binary system:-

$$J_A = Q_A (P_1 x - P_2 y_i)$$

x = feed composition

y_i = Composition at interface (skin)

$$J_B = Q_B [P_1 (1-x) - P_2 (1-y_i)]$$

The ratio of absolute pressure R

$$R = \frac{P_2}{P_1}$$

$$J_A = Q_A P_1 (x - R y_i)$$

$$J_B = Q_B P_1 [1 - x - R(1 - y_i)]$$

The local permeate composition y_i depends on the flux ratio at that point:-

$$y_i = \frac{J_A}{J_A + J_B} = \frac{q_A P_1 (x - R y_i)}{q_A P_1 (x - R y_i) + q_B P_1 [1 - x - R(1 - y_i)]}$$

using α for the permeability ratio q_A / q_B gives

$$y_i = \frac{x - R y_i}{x - R y_i + (1 - x - R + R y_i)/\alpha}$$

Rearrangements gives

$$(\alpha - 1) y_i^2 + \left(1 - \alpha - \frac{1}{R} - \frac{x(\alpha - 1)}{R}\right) y_i + \frac{\alpha x}{R} = 0 \quad \text{—(A)}$$

above equation shows how the local permeate composition depends on the pressure ratio, the selectivity, and the feed composition.

when $R \to 0$

$$y_i = \frac{x}{x + (1 - x)/\alpha}$$

or $$y_i = \frac{\alpha x}{1 + (\alpha - 1) x}$$

At a pressure ratio of 1 ($R = 1$), no separation occurs in a binary system, since there is no driving force for diffusion.

The composition of the permeate stream at any point along the separator is an integrated average of the incremental contribution to V

$$y = \frac{\sum \Delta V y_i}{V}$$

$$y = \frac{\int y_i \, dV}{V}$$

The overall and component material balances for the separator are

$$L_{in} = L_{out} + V_{out}$$

$$L_{in} x_{in} = L_{out} x_{out} + V_{out} y_{out}$$

When using a stepwise solution to determine the separator performance,

$$L_i = L_j + \Delta V \quad \text{— (b)}$$

$$L_i x_i = L_j x_j + \Delta V \bar{y} \qquad (\bar{y} = \text{avg composition})$$

$$\bar{y} = \frac{1}{2}(y_i + y_j)$$

replace $L_j = L_i - \Delta V$

$$L_i (x_i - x_j) = \Delta V(\bar{y} - x_j) \quad \text{— (c)}$$

equations A, b, c are solved numerically to determine the amount of permeate and its composition for chosen values of x_{out}.

The area needed for separation is calculated from the total flux or the flux of A

$$A = \sum \frac{\Delta V}{(J_A + J_B)}$$

$$A = \sum \left(\frac{\Delta V \bar{y}}{J_A} \right)$$

An approximate area can be obtained by:-

$$A = \frac{(Vy)_{out}}{(J_A)_{avg}} = \frac{(Vy)_{out}}{Q_A (P_1 x - P_2 y_i)_{avg.}}$$

Separator arrangements:-

① parallel, ② series, ③ two-stage flow or ④ continuous membrane column.

Membrane processes

SEPARATOR ARRANGEMENT

Single unit: Diameter = 1 ft, Length= 3 – 5 m

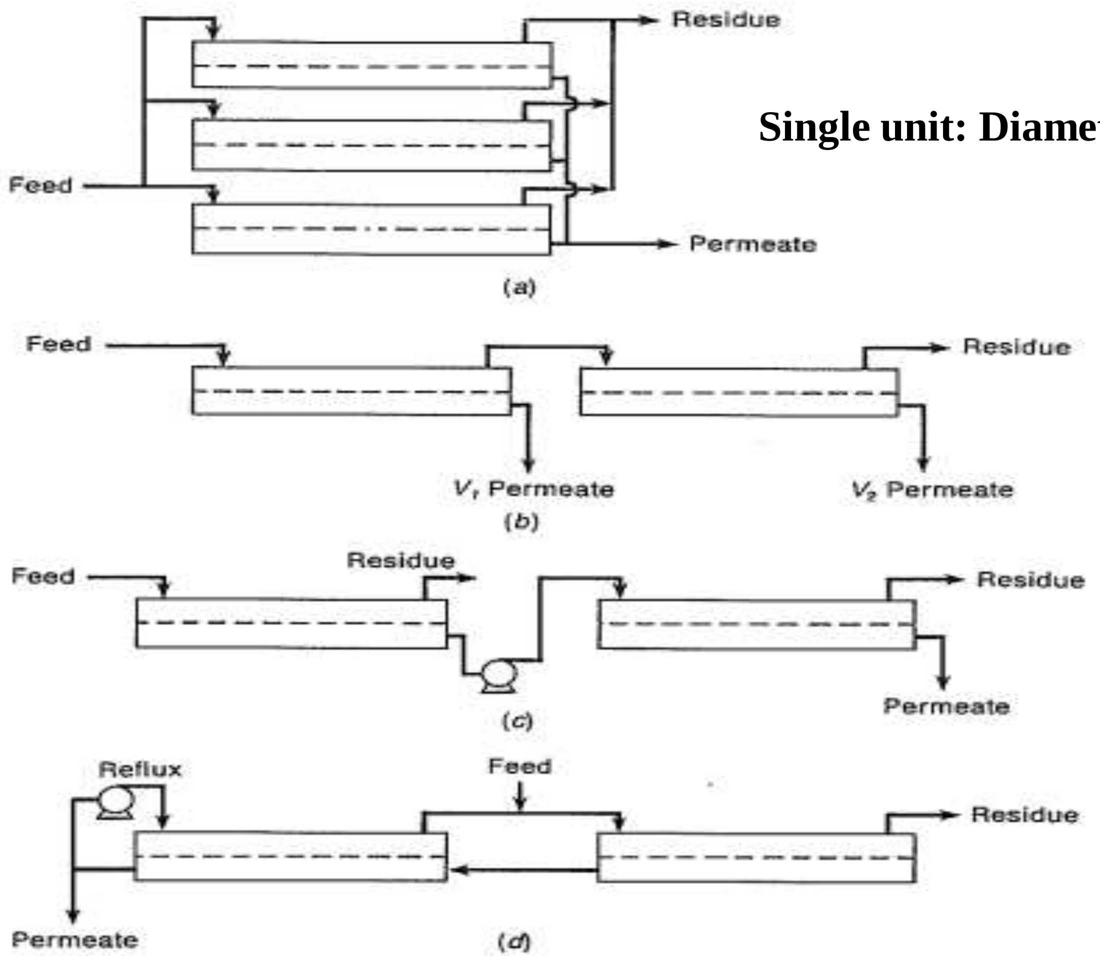


FIGURE 26.11
Separator arrangements: (*a*) parallel flow; (*b*) series flow; (*c*) two-stage flow; (*d*) continuous membrane column.

Membrane processes

- Microfiltration
- Ultrafiltration
- Reverse osmosis
- Gas separation/permeation
- Pervaporation
- Dialysis
- Electrodialysis

Characteristics of filtration processes

Process technology	**Separation principle**	**Size range**	**MWCO**	
MF	Size	0.1-1μm	-	
UF	Size,charge	1nm-100nm	>1000	
NF	Size, charge, affinity	1nm	200-1000	
RO	Size, charge, affinity	< 1nm	<200	

Process technology	**Typical operating pressure (bar)**	**Feed recovery (%)**	**Rejected species**
MF	0.5-2	90-99.99	Bacteria, cysts, spores
UF	1-5	80-98	Proteins, viruses, endotoxins, pyrogens
NF	3-15	50-95	Sugars, pesticides
RO	10-60	30-90	Salts, sugars

DIALYSIS

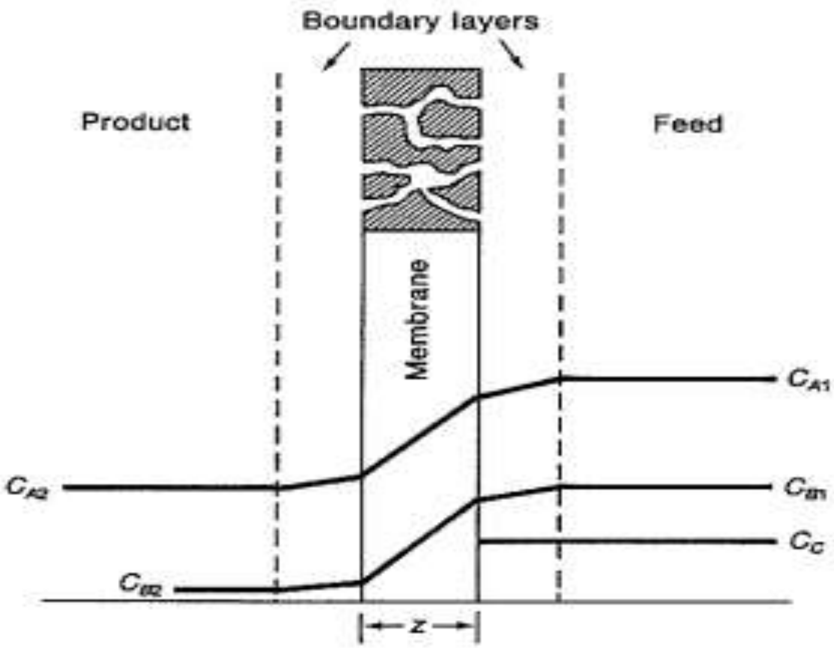


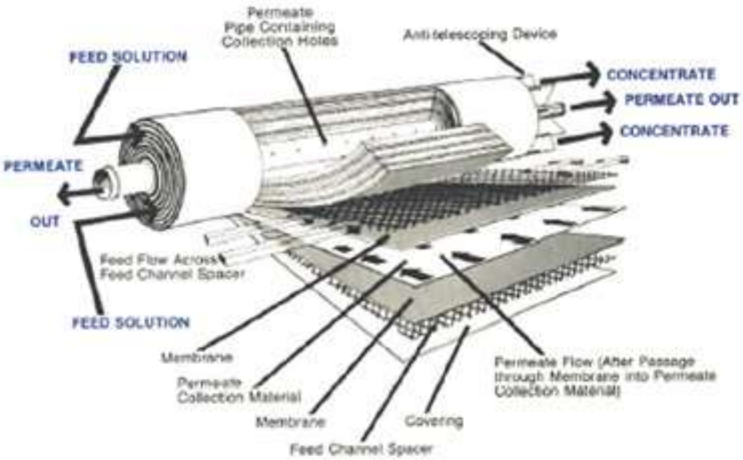
FIGURE 26.12
Concentration gradients in dialysis.

$$J_A = K_A(C_{A1} - C_{A2})$$

$$\frac{1}{K_A} = \frac{1}{k_{1A}} + \frac{1}{k_{mA}} + \frac{1}{k_{2A}}$$

$$k_m = \frac{D_e}{z}$$

Spiral wound module



Reverse osmosis

- Miscible solutions of different concentration separated by a membrane that is permeable to solvent but impermeable to solute. Diffusion of solvent occurs from less concentrated to a more concentrated solution where solvent activity is lower (osmosis).
- Osmotic pressure is pressure required to equalise solvent activities.
- If $P >$ osmotic pressure is applied to more concentrated solution, solvent will diffuse from concentrated solution to dilute solution through membrane (reverse osmosis).

Reverse osmosis

The permeate is nearly pure water at ~ 1atm. and very high pressure is applied to the feed solution to make the activity of the water slightly greater than that in the permeate. This provides an activity gradient across the membrane even though the concentration of water in the product is higher than that in the feed.

Reverse osmosis

- Permeate is pure water at 1 atm. and room temperature and feed solution is at high P.
- No phase change.
- Polymeric membranes used e.g. cellulose acetate
- 20 – 50 atm. operating pressure.
- Concentration polarisation at membrane surface.

Water flux

$$\mathbf{Jw = \frac{c_w D_w v_w}{RT} \frac{(\Delta P - \Delta\pi)}{z}}$$

D_w is diffusivity in membrane, $cm^2\ s^{-1}$

c_w is average water conc. in membrane, $g\ cm^{-3}$ (~ 0.2)

v_w is partial molar volume of water, $cm^3 g^{-1}$

ΔP pressure difference

R gas constant

T temperature

$\Delta\pi$ osmotic pressure

z membrane thickness

Salt flux

$$J_s = D_s S_s \frac{(\Delta c_s)}{z}$$

Ds diffusivity

Ss solubility coefficient

Δc_s difference in solution concentration