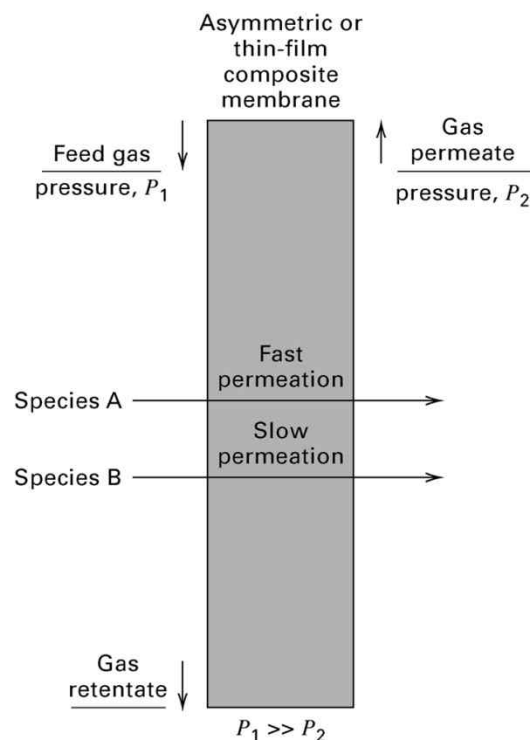# Lecture 14.
Membrane Separation Processes (2)

- Gas Permeation
  - Operation
  - Major applications

- Pervaporation
  - Major applications
  - Pervaporation processes
  - Materials and modules
  - Models for permeant transport

Gas Permeation (1)

- Low-molecular-weight species (MW < 50) are separated from small amounts of higher-molecular-weight species in feed gas
- The membrane, often dense but sometimes microporous, is permselective for the low-molecular-weight species
- Permselectivity depends on both membrane absorption and transport rate

Asymmetric or thin-film composite membrane

Feed gas pressure, P_1

Gas permeate pressure, P_2

Fast permeation

Slow permeation

Species A

Species B

Gas retentate

$P_1 >> P_2$

- Solution-diffusion model (partial-pressure or fugacity driving force)

$$N_i = \frac{H_i D_i}{l_M}(p_{i_F} - p_{i_P}) = \frac{P_{M_i}}{l_M}(p_{i_F} - p_{i_P})$$

- The products are a permeate enriched in A and a retentate enriched in B
- A near-perfect separation is generally not achievable
- If the membrane is microporous, pore size is extremely important because it is necessary to block the passage of species B

Gas Permeation (2)

- Since the early 1980s, applications of gas permeation with dense polymeric membranes have increased dramatically
- Since 1986, the most rapidly developing application for gas permeation has been air separation, for which available membranes have separation factors for O_2 with respect to N_2 of 3 to 7
- Gas permeation is also favorable for H_2 recovery due to high separation factors. The rate of permeation of H_2 is more than 30 times that for N_2
- Major applications
  (1) Separation of H_2 from CH_4
  (2) Adjustment of H_2–to–CO ratio in synthesis gas
  (3) O_2 enrichment of air
  (4) N_2 enrichment of air
  (5) Removal of CO_2
  (6) Drying of natural gas and air
  (7) Removal of helium
  (8) Removal of organic solvents from air

Permeate

Compressed Air

Nitrogen 93 - 99.9 %

| H_2O | H_2 | He | CO_2 | O_2 | Ar | N_2 | CH_4 |

Fast
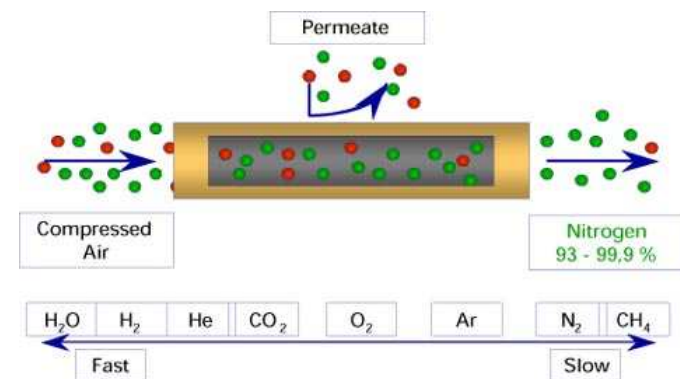
Slow

Gas Permeation (3)

- Advantages of gas permeation compared to other separation techniques
  - low capital investment, ease of installation, ease of operation, absence of rotating parts, high process flexibility, low weight and space requirements, and low environmental impact
  - if the feed gas is already high pressure, a gas compressor is not needed
- Almost all large-scale applications for gas permeation use spiral-wound or hollow-fiber modules because of their high packing density
- Feed-side pressure is typically 300 to 500 psia, but can be as high as 1,650 psia
- When the feed contains condensables, it may be necessary to preheat the feed gas to prevent condensation as the retentate becomes richer in the high-molecular-weight species
- For high-temperature applications where polymers cannot be used, membranes of glass, carbon, and inorganic oxides are available, but are limited in their selectivity

Pervaporation (1)

- Pervaporation: a membrane technical method for the separation of mixtures of liquids by partial vaporization through a non-porous or porous membrane
- The phase on one side of the pervaporation is different from that on the other
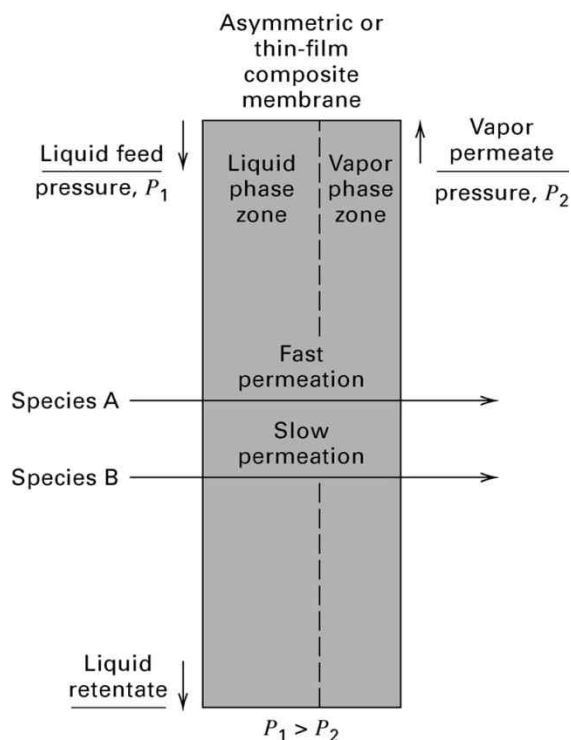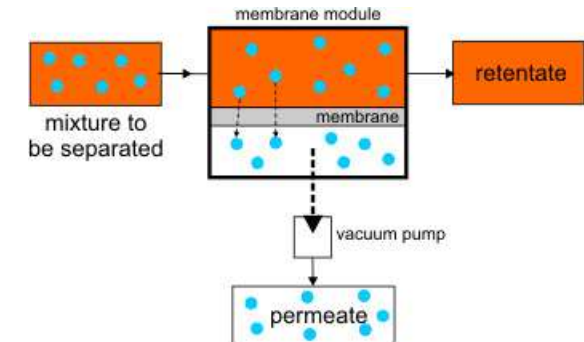
- Feed to the membrane module is a liquid mixture at pressure P_1, which is high enough to maintain a liquid phase
- The permeate side pressure P_2, which may be a vacuum, is held at or below the dew point of the permeate, making it vapor
- A composite membrane is used that is selective for species A, but with some finite permeability for species B
- The dense, thin-film side of the membrane is in contact with the liquid side

Pervaporation (2)

- History of pervaporation
  - In 1917, the term of pervaporation was first reported
  - In 1961, the economical potential of pervaporation was shown
  - Mid 1970s, commercial applications were possible, when adequate membrane materials became available
- Major applications
  (1) Dehydration of ethanol
  (2) Dehydration of other organic alcohols, ketones, and esters
  (3) Removal of organics from water
  (4) Separation of close-boiling organic mixtures like benzene-cyclohexane
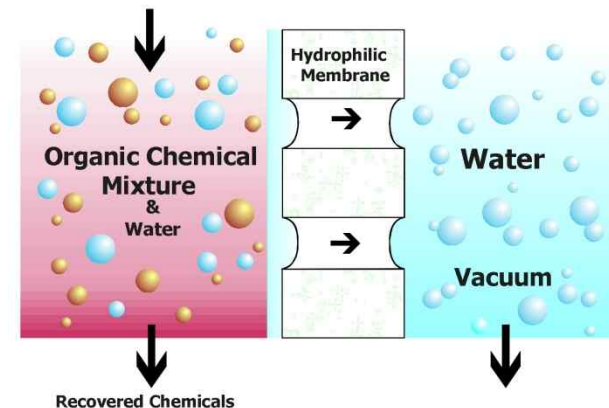

- Pervaporation is favored when the feed solution is dilute in the main permeant because sensible heat of the feed mixture provides the permeant enthalpy of vaporization
- If the feed is rich in the main permeant, a number of membrane stages may be needed, with a small amount of permeant produced per stage and reheating of the retentate between stages
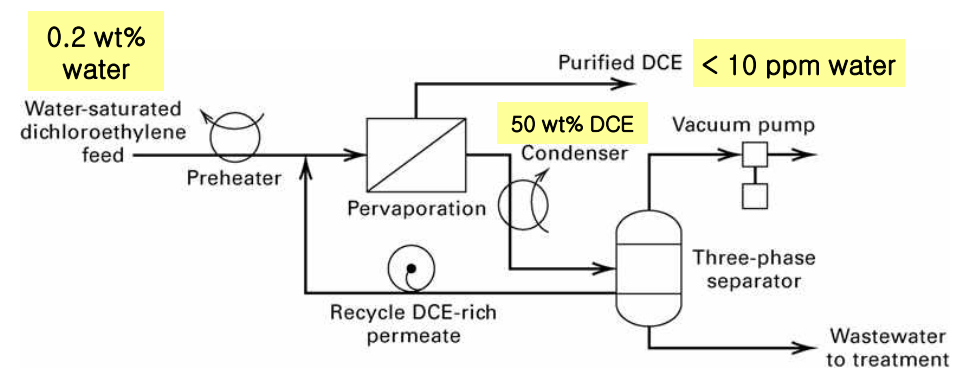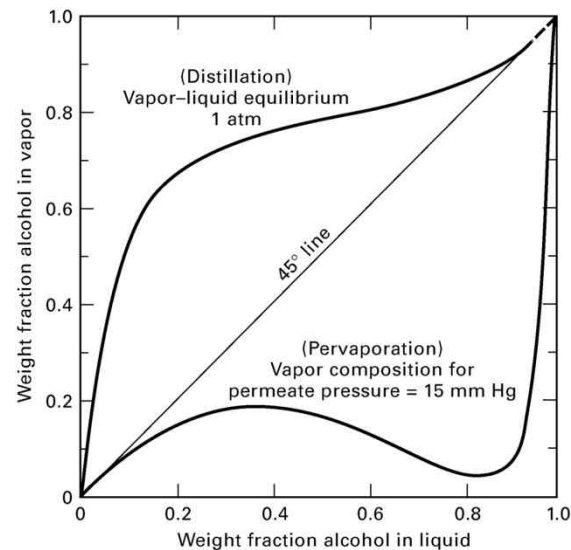
Pervaporation (3)

- Pervaporation processes

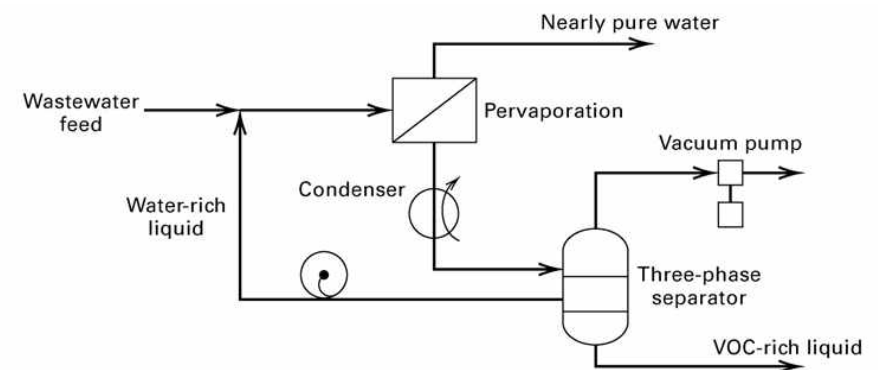Hybrid process for removal of water from ethanol

95 wt% ethanol

99.5 wt% ethanol

25 wt% ethanol

60 wt% ethanol
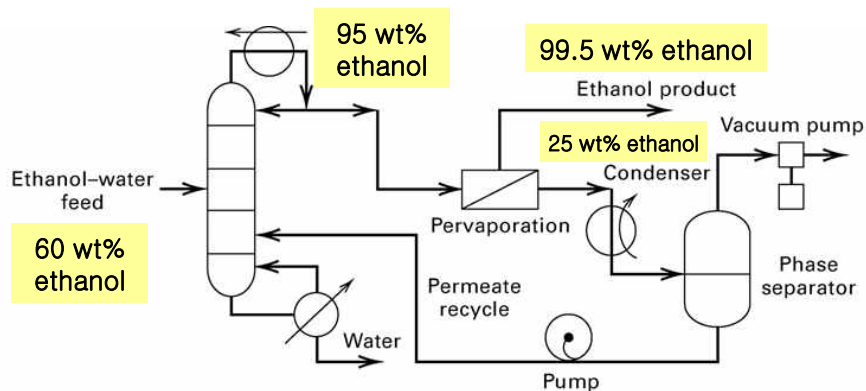
Dehydration of dichloroethylene

0.2 wt% water

< 10 ppm water

50 wt% DCE

Comparison of ethanol–water separabilities

Removal of volatile organic compounds (VOCs) from wastewater

Pervaporation (4)

- For water permeation, hydophilic membrane materials are preferred

- A three-layer composite membrane (porous polyester support layer, microporous poly-acrylonitrile or polysulfone membrane, dense PVA) is used for the dehydration of ethanol: chemical and thermal stability with adequate permeability

- Hydrophobic membranes, such as silicone rubber and Teflon, are preferred when organics are the permeating species

- Commercial membrane modules for pervaporation

  - Plate-and-frame type (almost exclusively): because of the ease of using gasketing materials that are resistant to organic solvents and the ease of providing heat exchange for vaporization and high-temperature operation

  - Hollow-fiber modules: used for removal of VOCs from wastewater; because feeds are generally clean and operation is at low pressure, membrane fouling and damage is minimal, resulting in a useful membrane life of 2-4 years

Pervaporation (5)

- A pervaporation module may operate with heat transfer or adiabatically, with the enthalpy of vaporization supplied by feed enthalpy

- Heat balance in pervaporation

$$(m_{A_F} C_{P_A} + m_{B_F} C_{P_B})(T_F - T_0)$$

$$= [(m_{A_F} - m_{A_P})C_{P_A} + (m_{B_F} - m_{B_P})C_{P_B}](T_R - T_0)$$

$$+ (m_{A_P} C_{P_A} + m_{B_P} C_{P_B})(T_P - T_0)$$

$$+ m_{A_P} \Delta H_A^{\text{vap}} + m_{B_P} \Delta H_B^{\text{vap}}$$

The enthalpies of vaporization are evaluated at T_p (dew point at the permeate vacuum upstream of the condenser)

$$(m_{A_F} C_{P_A} + m_{B_F} C_{P_B})(T_F - T_R)$$

$$= (m_{A_P} C_{P_A} + m_{B_P} C_{P_B})(T_P - T_R)$$

$$+ m_{A_P} \Delta H_A^{\text{vap}} + m_{B_P} \Delta H_B^{\text{vap}}$$

Pervaporation (6)

- Models for permeant transport based on partial-vapor-pressure

  Because pressures on both sides of the membrane are low, the gas phase follows the ideal-gas law

  $$a_i^{(1)} = f_i^{(1)} / f_i^{(0)} = p_i^{(1)} / P_i^{s(1)}$$

  Liquid on the upstream side of the membrane is generally nonideal

  $$a_i^{(1)} = \gamma_i^{(1)} x_i^{(1)} \implies p_i^{(1)} = \gamma_i^{(1)} x_i^{(1)} P_i^{s(1)}$$

  On the vapor side of the membrane (2)

  $$p_i^{(2)} = y_i^{(2)} P_P^{(2)}$$

  Driving force: $\left(\gamma_i^{(1)} x_i^{(1)} P_i^{s(1)} - y_i^{(2)} P_P^{(2)} \right)$

  Permeant flux

  $$N_i = \frac{P_{M_i}}{l_M} \left(\gamma_i x_i P_i^s - y_i P_P \right) \qquad N_i = \bar{P}_{M_i} \left(\gamma_i x_i P_i^s - y_i P_P \right)$$