Gas permeation

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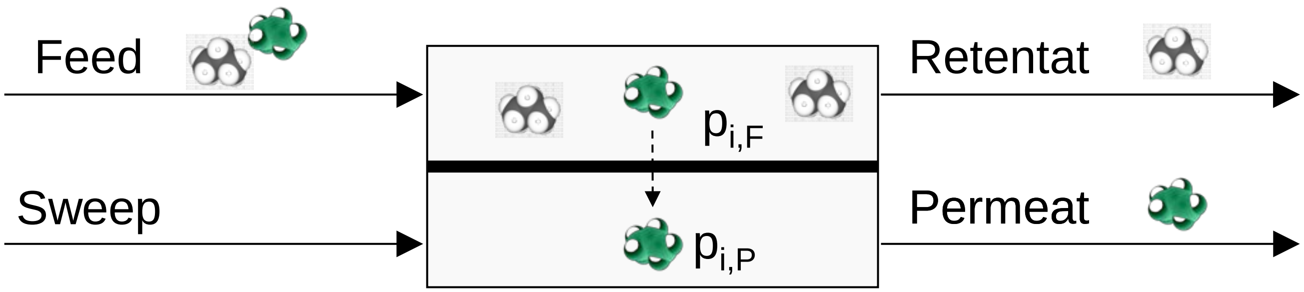
What is gas permeation?



Gas permeation is the art of walking through an apparently dense wall ....

What is gas permeation?

- Gas Permeation (GP): the separation of gases with membranes

- GP is a promising alternative to conventional techniques, like:
  - rectification at low temperatures
  - physical or chemical absorption
  - adsorption on activated carbon or zeolites

- Advantages:
  - easy, flexible, mobile, space-saving units
  - low energy consumption

Overview

- Materials & separation mechanisms
  - Mesoporous membranes
  - Microporous membranes
  - Dense membranes
- Parameters describing the transport properties
- Membranes & modules
- Plant design
- Applications
- Future directions
- Conclusion

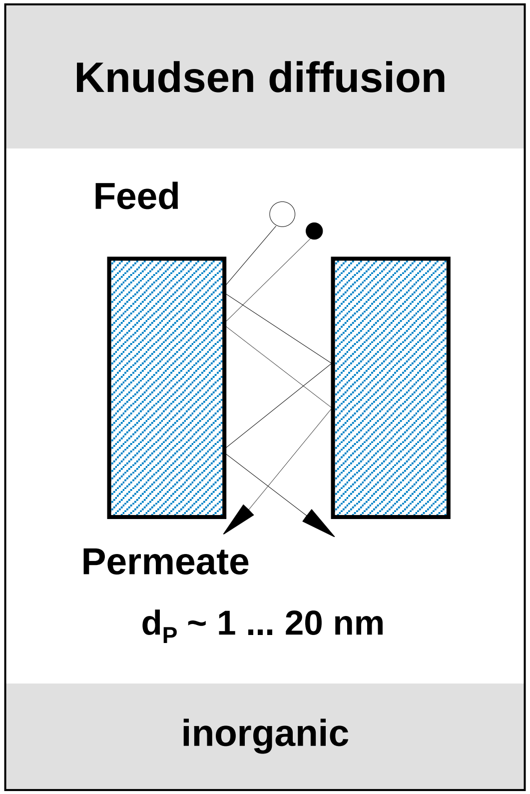
Membrane materials

Basically all materials which you can convert to thin, stable films

- Polymers
  - polysulphone
  - polyimide
  - polyaramide
  - polycarbonate
  - cellulose acetate
  - polyphenylene oxides
  - silicones

- Inorganic Materials
  - metal
  - glass
  - ceramics

Mesoporous membranes



d_P > 20 nm: viscous flow without selectivity

- Knudsen diffusion:

  Transport based on the dominance of gas/wall - interactions

$$Kn = \frac{\lambda}{d_p} >> 1$$

- Knudsen number >> 1

- mole fluxes: $$\dot{n}_i'' = \frac{4\,\varepsilon\, d_p}{3\tau\sqrt{2\pi R T M_i}} \frac{\Delta p_i}{\delta}$$

- ideal separation factor : $$\alpha_{ij} = \sqrt{\frac{M_j}{M_i}} \quad (p_{Pi,j} \to 0)$$

➡ Separation depends on difference in molecular masses

➡ Ideal separation factor is rather low

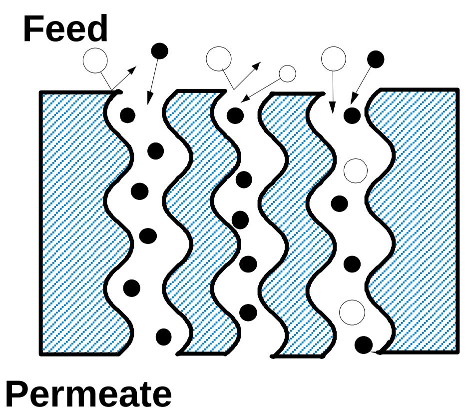
$\alpha_{O2/N2} = (28/32)^{1/2} = 0{,}935$

Microporous membranes

- Molecular sieve separation based on molecule sizes & adsorption effects

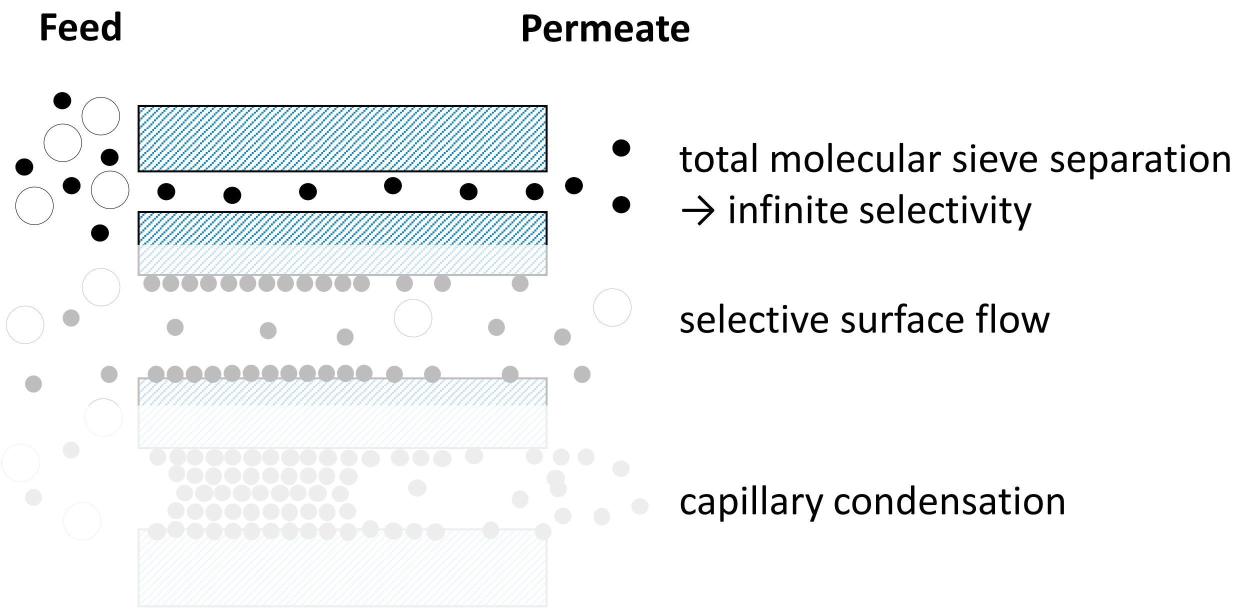
$$\frac{d_{molecule}}{d_p} \approx 1$$

Molecular sieve



d_P ~ 0.3 ... 10 nm

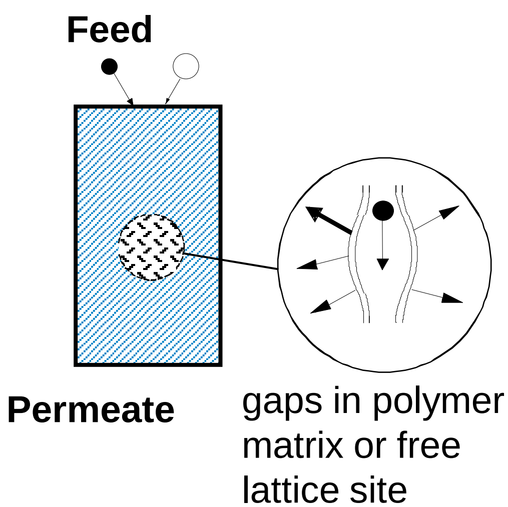
inorganic



➡ selectivity is very sensitive to defects/pinholes

Dense membranes

Solution-Diffusion-Model



mainly polymers
also inorganic

- Selective due to difference in solubility and diffusivity

Generalised Fick's Law of diffusion

$$\dot{n}_i'' = -c_{iM} \frac{D_{iM,0}}{RT} \frac{\partial \mu_{iM}}{\partial z}$$

assuming:

1. non-coupled permeate fluxes
2. Henry's Law: $c_i = S_i\, p_i$
3. chemical potential at the membrane surface equals one in the gas phase

linear mass transport equation

$$\boxed{\dot{n}_i'' = Q_i\left(p_{i,F} - p_{i,P}\right) = Q_i\left(x_i p_F - y_i p_P\right)}$$

Q_i: permeance
membrane and species specific

application
specific

Solution-Diffusion-Model

- Permeance Q_i (dt. Permabilität):
  - membrane and species specific
  - units: $\left[\frac{m^3}{m^2 \cdot h \cdot bar}\right] or \left[GPU\right]$

$$Q_i = \frac{D_i \cdot S_i}{\delta} = \frac{\text{Diffusion coefficient} \cdot \text{solubility coefficient}}{\text{active layer thickness of membrane}}$$

- Permeability P_i (dt. intrisische Permeabilität):
  - material specific
  - independent of membrane thickness
  - units: $\left[\frac{m^3 \cdot m}{m^2 \cdot h \cdot bar}\right] or \left[barrer\right]$

$$P_i = D_i \cdot S_i$$

Solution-Diffusion-Model

Selectivity (Solution-Diffusion-Model)

- Selectivity:

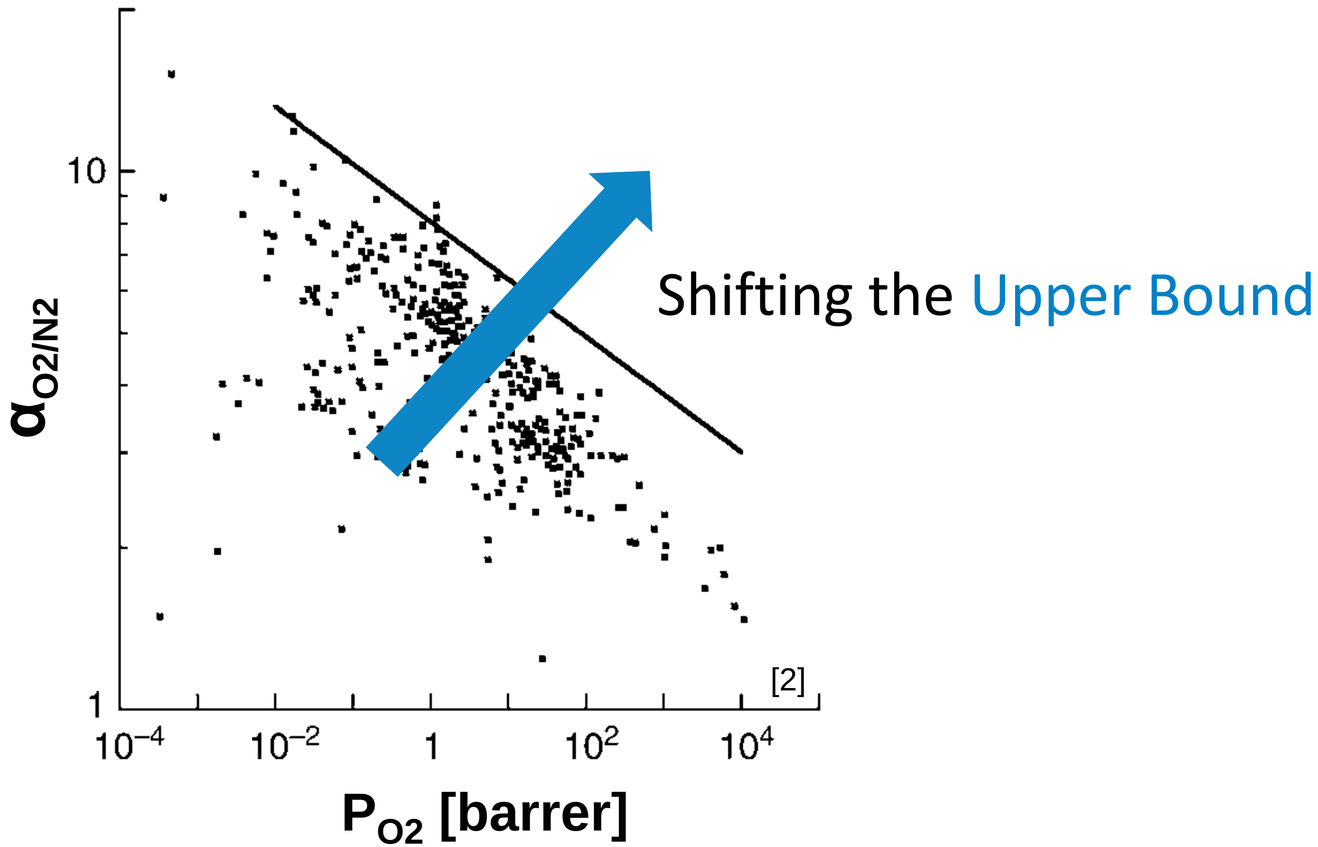
$$\alpha_{ij} = \frac{Q_i}{Q_j} = \underbrace{\left(\frac{D_i}{D_j}\right)}_{\text{diffusion selectivity}} \underbrace{\left(\frac{S_i}{S_j}\right)}_{\text{solubility selectivity}}$$

- Recommendations for an ideal membrane
  - ($D_i \cdot S_i$) for component *i* as large as possible
  - ($D_j \cdot S_j$) for component *j* as low as possible
  - δ as low as possible

- In general:
  - Small molecules diffuse faster
  - Large molecules are more soluble

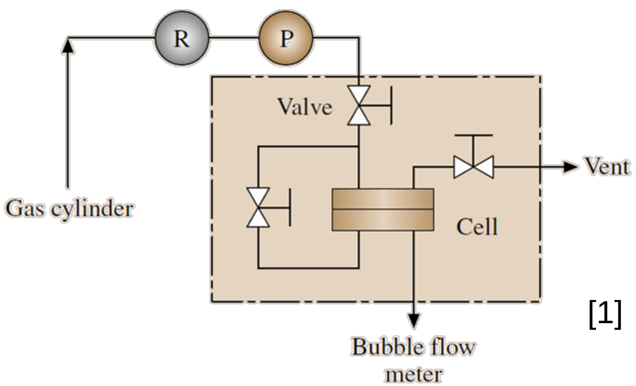
Robeson plot - α vs. P_i

- Permeablity/permeance and separation factor oppose each other



Experimental determination of Q

- Constant pressure – variable volume



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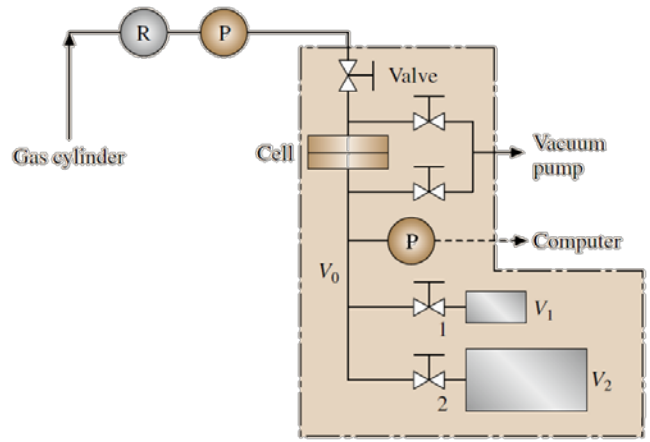
- Constant volume – variable pressure



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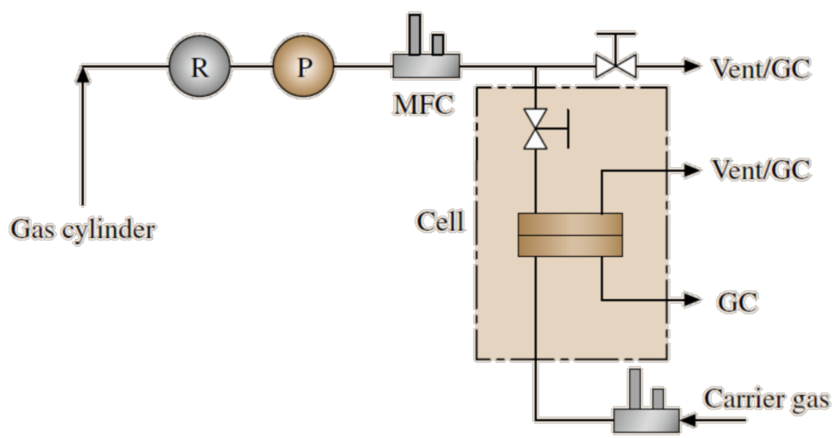
pure gas

- Gas chromatograph



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mixed gas

Overview

- Materials & separation mechanisms
- Parameters describing the transport properties
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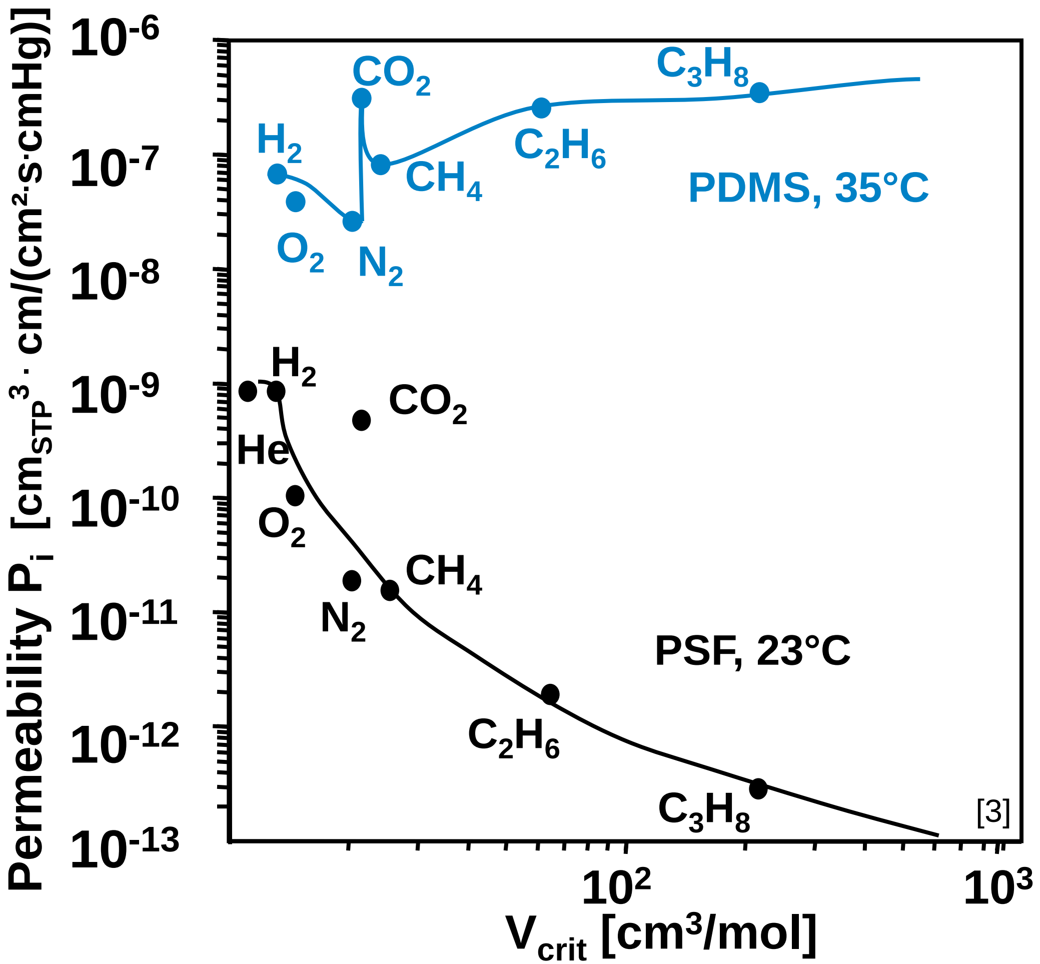
Influencing factors

- Materials
- Molecular properties
- Process parameters

Permeability



rubbery ($T > T_g$)

selective for vapours
-> solvent recovery

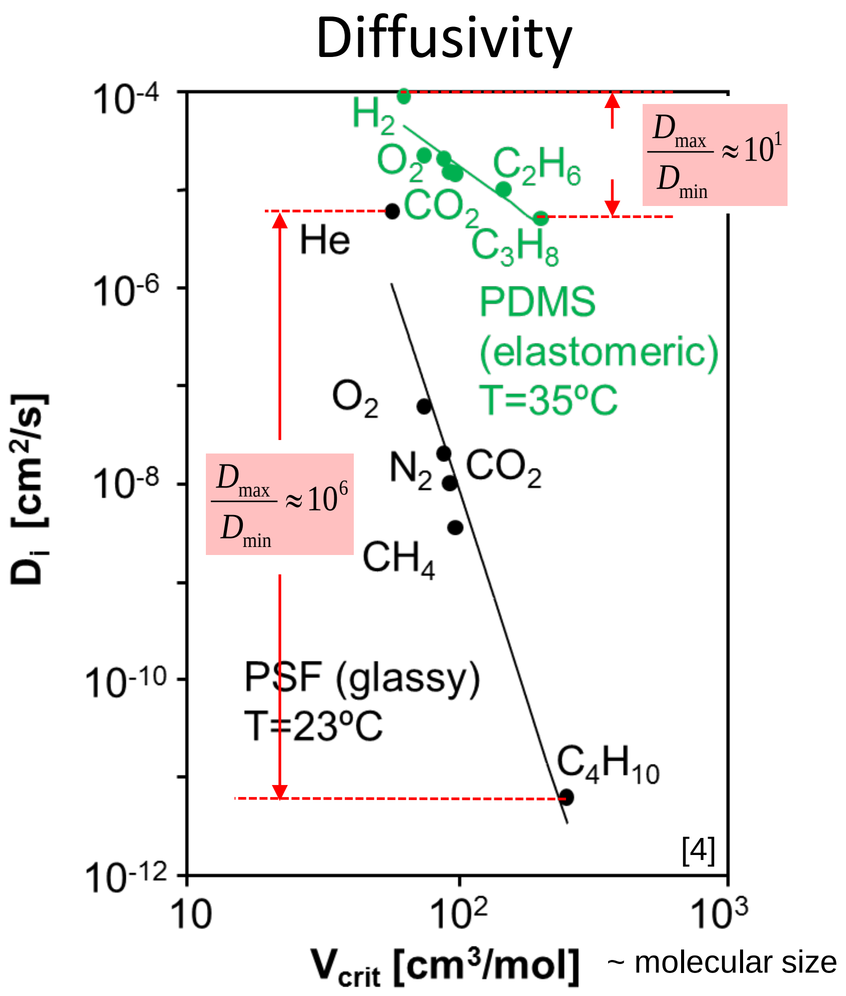
$P_{rubbery} > P_{glassy}$

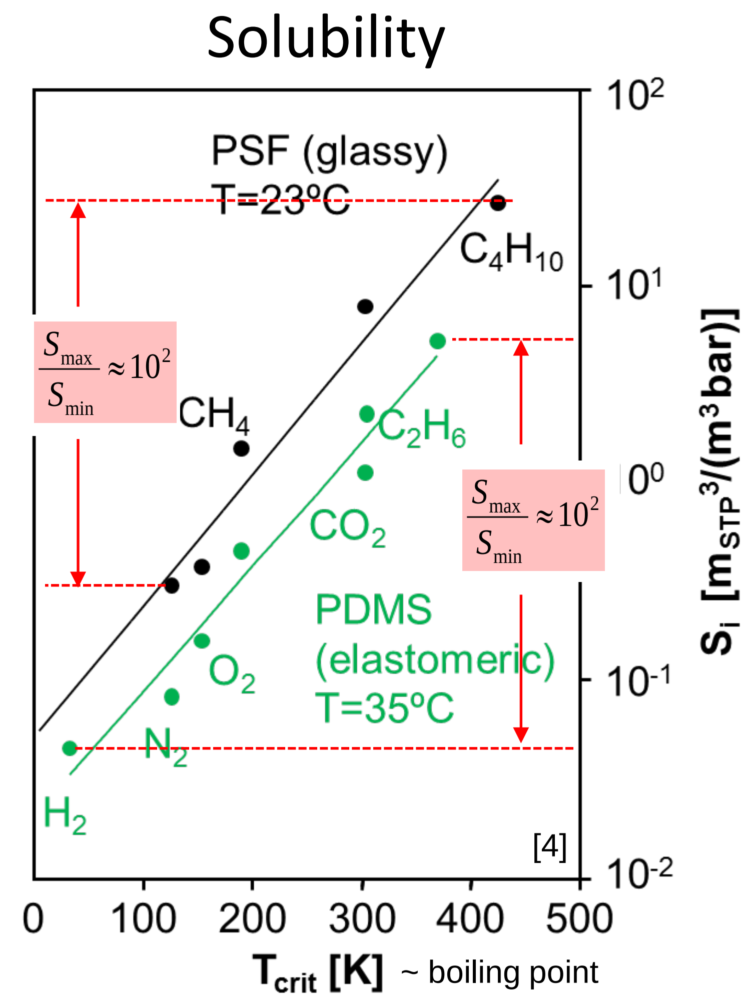
glassy membranes ($T<T_g$)

selective for permanent gases
-> separation of N_2/O_2, CH_4/CO_2

T_g - glass transition temperature

Diffusivity vs. Solubility





→ small molecules diffuse faster

→ condensabel gases are more soluble

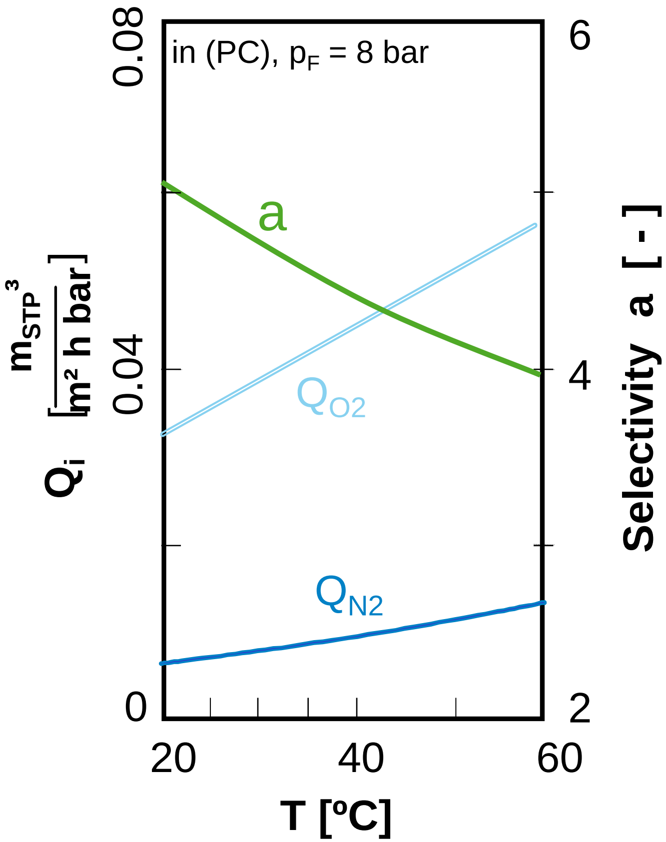
Take home - polymers / molecules

- glassy polymers ($T_{Process} < T_g$)
  - high influence of molecular size on diffusion coefficient
  - diffusivity determines selectivity
  - typical applications: N_2/O_2-separation, CH_4/CO_2 -separation

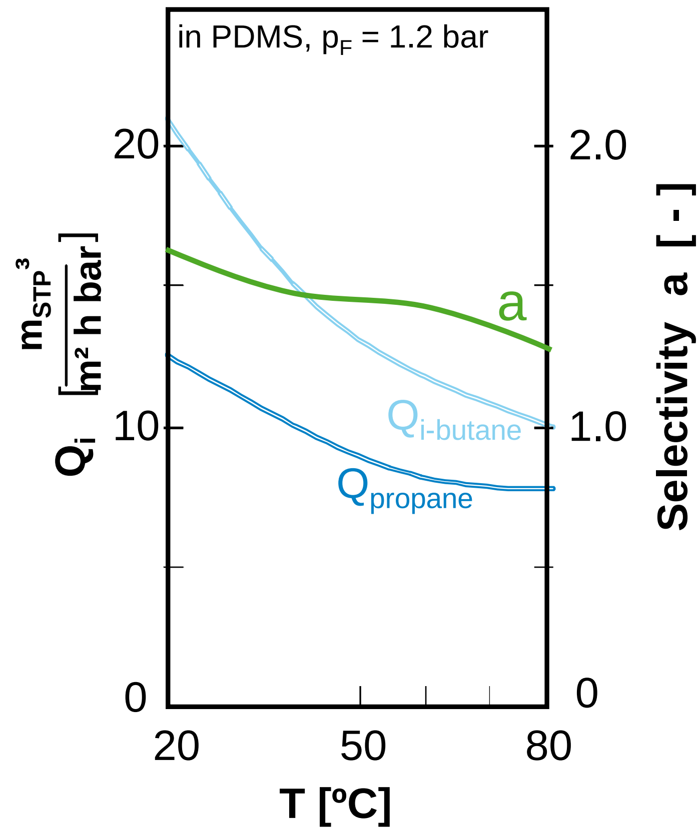
- rubbery polymers ($T_{Process} > T_g$)
  - $D_{rubbery}/D_{glassy}$: 100-100000
  - solubility determines the selectivity
  - typical applications: solvent recovery from off-gas

Permeability - operating temperature

permanent gases



vapors



T ↑ = selectivity↓

Permeability - operating pressure

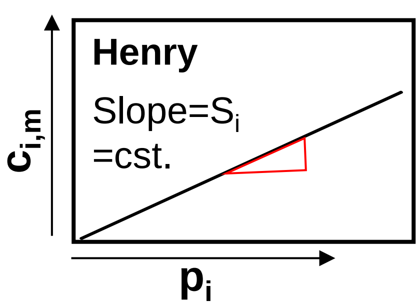
Absolute pressure

- membrane compaction (mechanically):
  - $p_i\uparrow \rightarrow D_i\downarrow \rightarrow Q_i\downarrow$

Partial pressure

- sorption

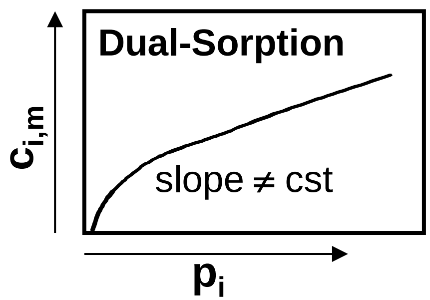
Ideal gas



no pressure dependence

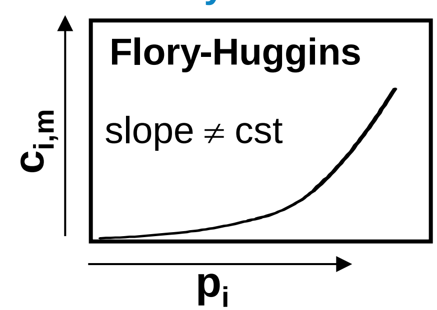
Real gas

glassy



$p_i\uparrow \rightarrow S_i\downarrow \rightarrow Q_i\downarrow$

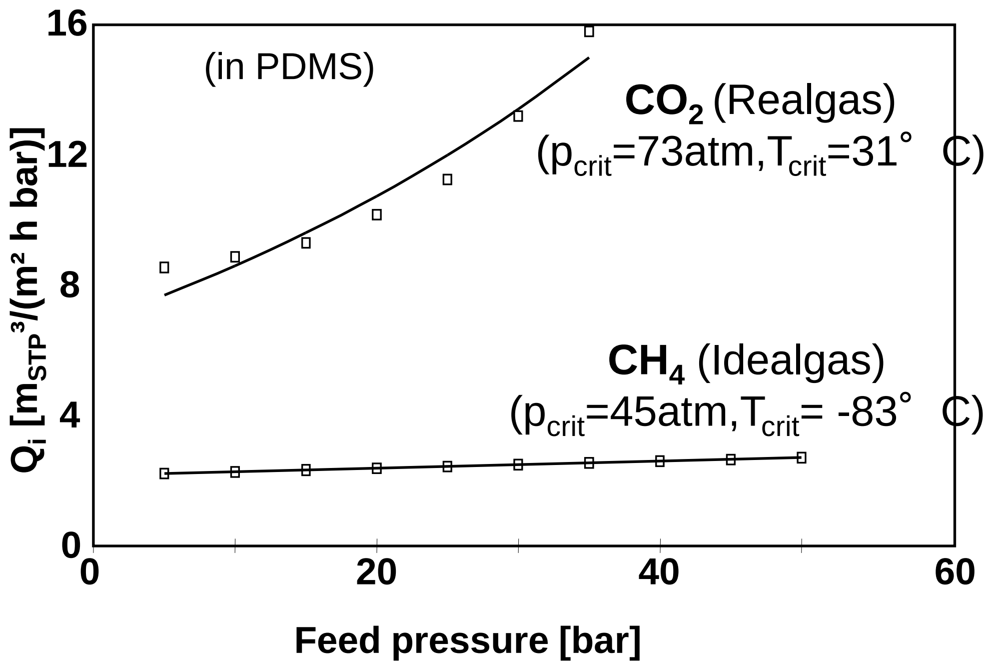
rubbery



$p_i\uparrow \rightarrow S_i\uparrow \rightarrow Q_i\uparrow$

Permeability - operating pressure

- membrane swelling (plasticization):
  - $p_i\uparrow \rightarrow D_i\uparrow \rightarrow Q_i\uparrow$



- mixed gas selectivity is often far below pure gas performance

$S_{mixed} < S_{pure}$

Overview

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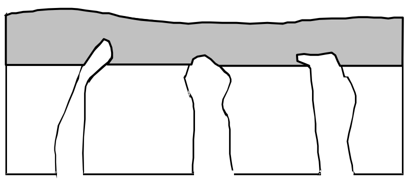
Membrane concepts

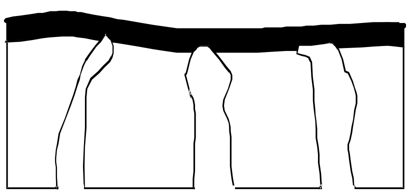
Loeb-Sourirajan membrane:



active layer (same polymer as support)

porous support

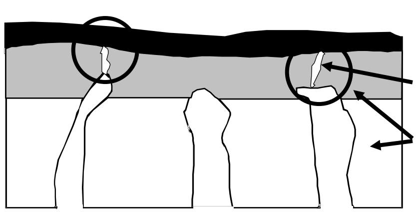
Ward-Riley composite membrane:



active layer (different polymer than support)

porous support

coated Loeb-Sourirajan membrane:



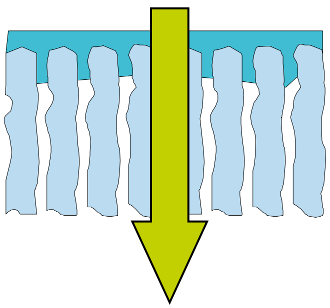
Dense coating (silicone)

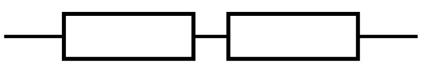
defects in active layer

active layer +support

Membrane Resistances

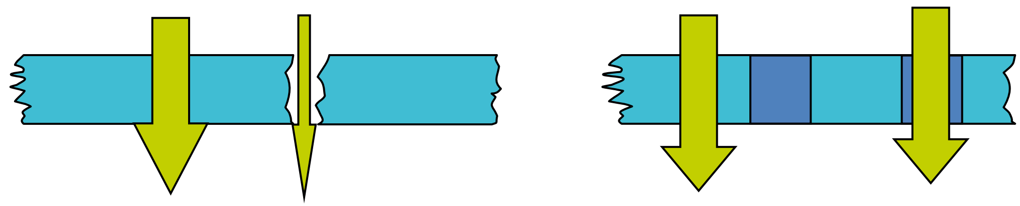
- Serial Resistance





$$R_{tot} = R_{AL} + R_{Supp}$$

- Parallel Resistance



$$\frac{1}{R_{tot}} = \frac{1}{R_{AL}} + \frac{1}{R_{pin\,hole}}$$

Membrane resistance in GP

- Analogy between electrical current and flux

Flux

$$Q_i = \frac{P_i A \Delta c_i}{l}$$

$$Q_i = \frac{\Delta c_i}{R_i} \quad \Longleftrightarrow \quad I = \frac{U}{R}$$

Current

with $$R_i = \frac{l}{P_i A}$$

Membrane resistance in GP

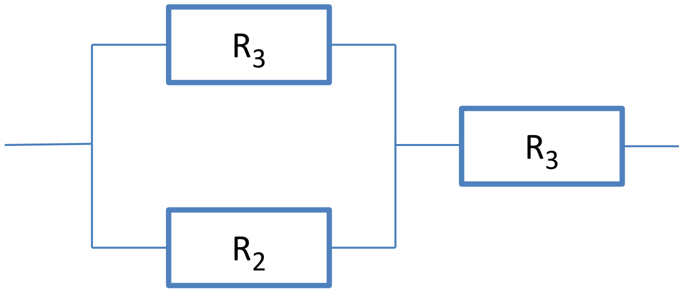
Total resistance

$$R_t = \frac{R_2 R_3}{R_2 + R_3} + R_4$$

R_2: Dense membrane

R_3: Pore resistance

R_4: Porous matrix



Membrane resistance in GP

Total resistance

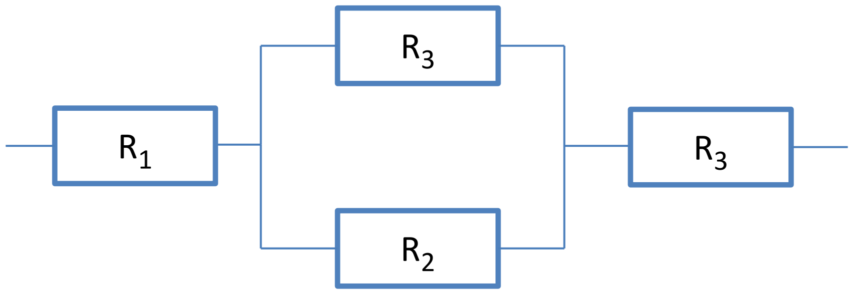
$$R_t = R_1 + \frac{R_2 R_3}{R_2 + R_3} + \underbrace{R_4}_{\approx 0}$$

R_1: Dense Coating

R_2: Dense membrane

R_3: Dense Coating in pores

R_4: Porous matrix



Criterias for modules

- high packing density
- small pressure loss (especially when operating with vacuum)
- mechanical, thermal, chemical stability
- economic production

Module concepts

packing density

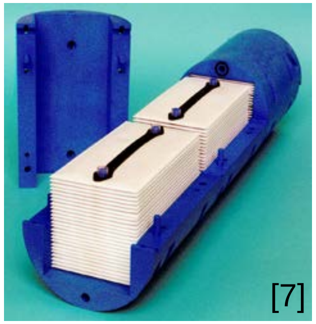
Δp

pre-cleaning

hollow fiber/
capillary

spiral wound

cushion



specific cost/m²

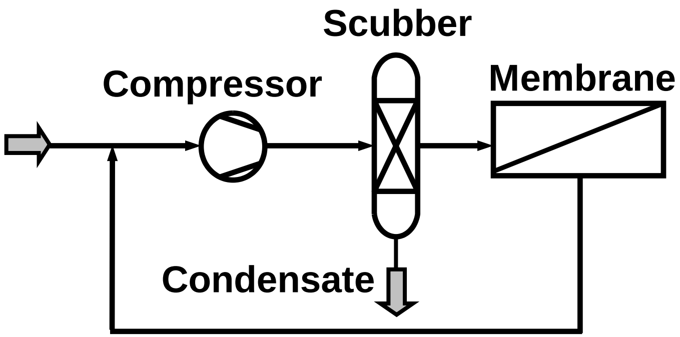
variety material

Overview

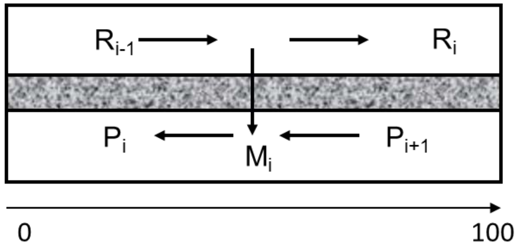
- Materials & separation mechanisms
- Parameters describing the transport properties
- Membranes & modules
- Plant design
  - Local mass transfer
  - Module performance
- Applications
- Future directions
- Conclusion

Plant design

Complete process-modelling (e.g. AspenPlus®, Pro2, etc.)

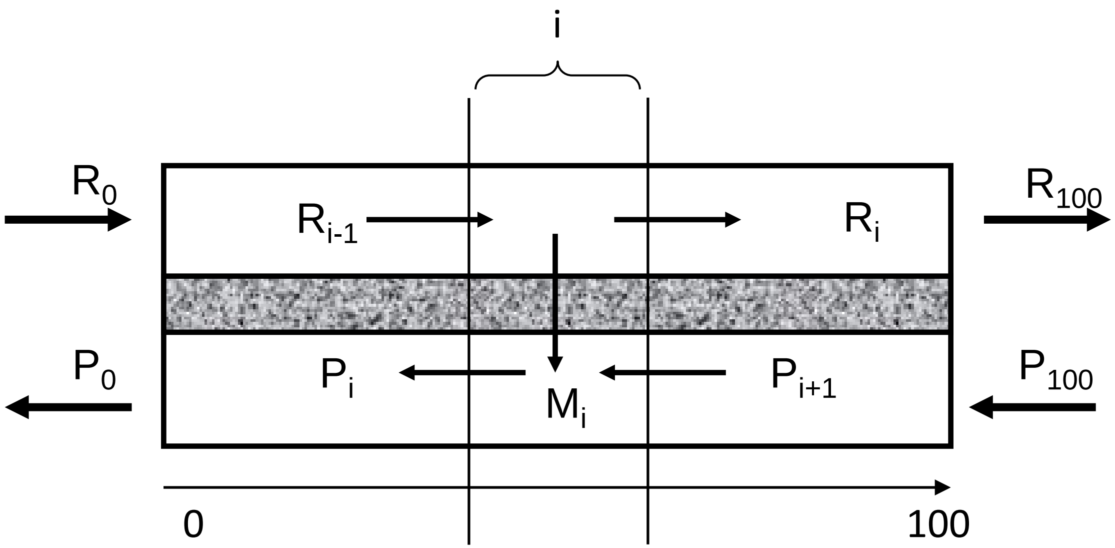


„Stand-alone"-calculation of module performance (e.g. Fortran, C++, Matlab, etc.)



Model for local mass transport

Discretization



- Multiple component system:
  numerical solution for differential equations
- Two component system:
  analytical solution

Binary mixtures

- Starting with the linear mass transfer equation... $\dot{n}_i'' = Q_i(x_i p_F - y_i p_P)$

...using following assumptions...

1. no concentration polarisation
2. no pressure drop in porous support layer
3. "unhindered" permeate flow (no influence of the flow pattern)

$$y_i = \frac{\dot{n}_i''}{\dot{n}_i'' + \dot{n}_j''}$$

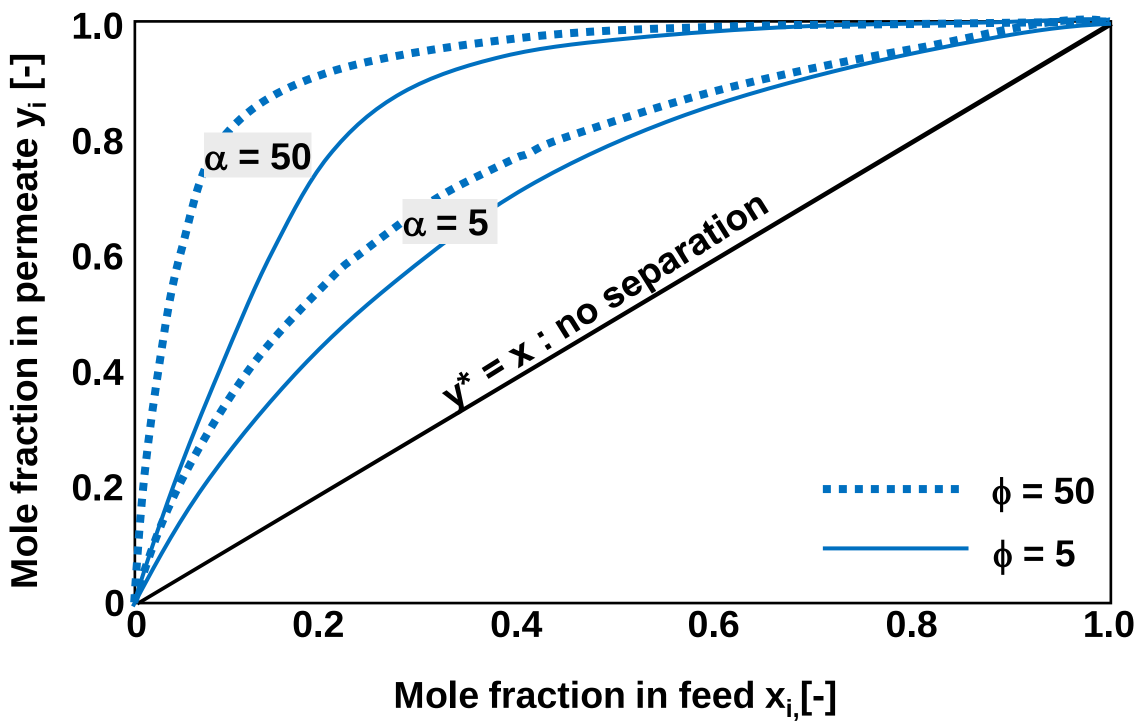
...yields the <u>local</u> permeate composition of a binary mixture

$$y_i = \frac{\alpha(x_i\phi - y_i)}{\alpha(x_i\phi - y_i) + (1 - x_i)\phi - (1 - y_i)} = f(x_i, \alpha, \phi)$$

- $\phi = p_{Feed} / p_{Permeate}$ = *pressure ratio > 1*
- α = *ideal separation factor > 1*
- x_i , y_i *are the mole fractions of the faster permeating species in the feed and permeate*

Binary mixtures

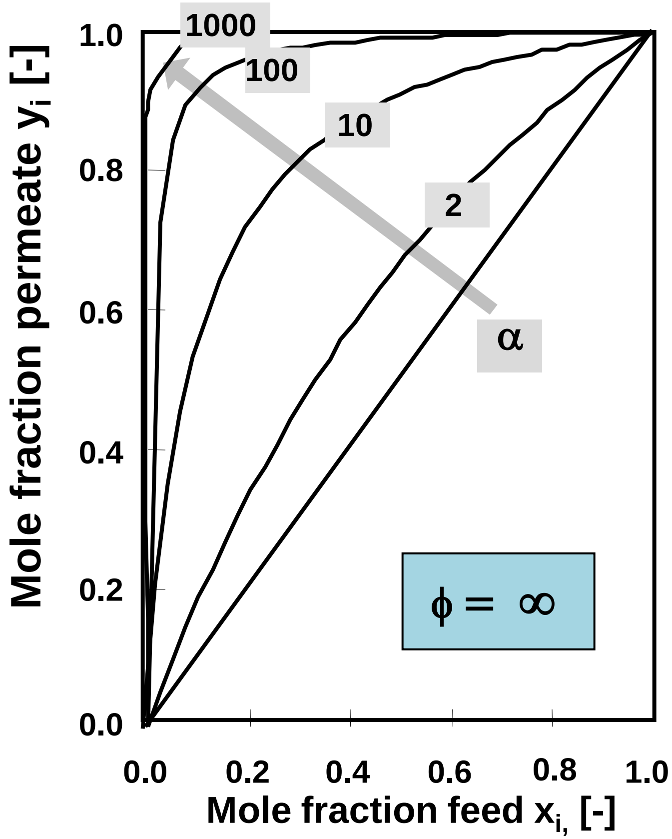
$$y_i = \frac{1}{2}\left(1+\phi\left(x_i + \frac{1}{\alpha - 1}\right)\right) - \sqrt{\left[\frac{1}{2}\left(1+\phi\left(x_i + \frac{1}{\alpha - 1}\right)\right)\right]^2 - \frac{\alpha \cdot \phi \cdot x_i}{\alpha - 1}}$$



pressure ratio Φ ↑
selectivity α ↑
} separation ↑

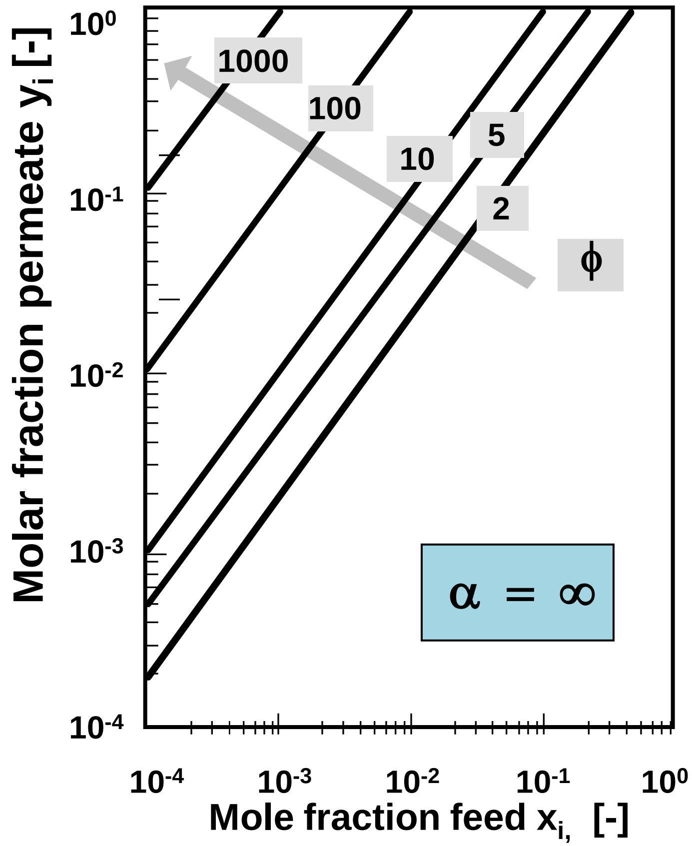
Binary mixtures

infinite driving force



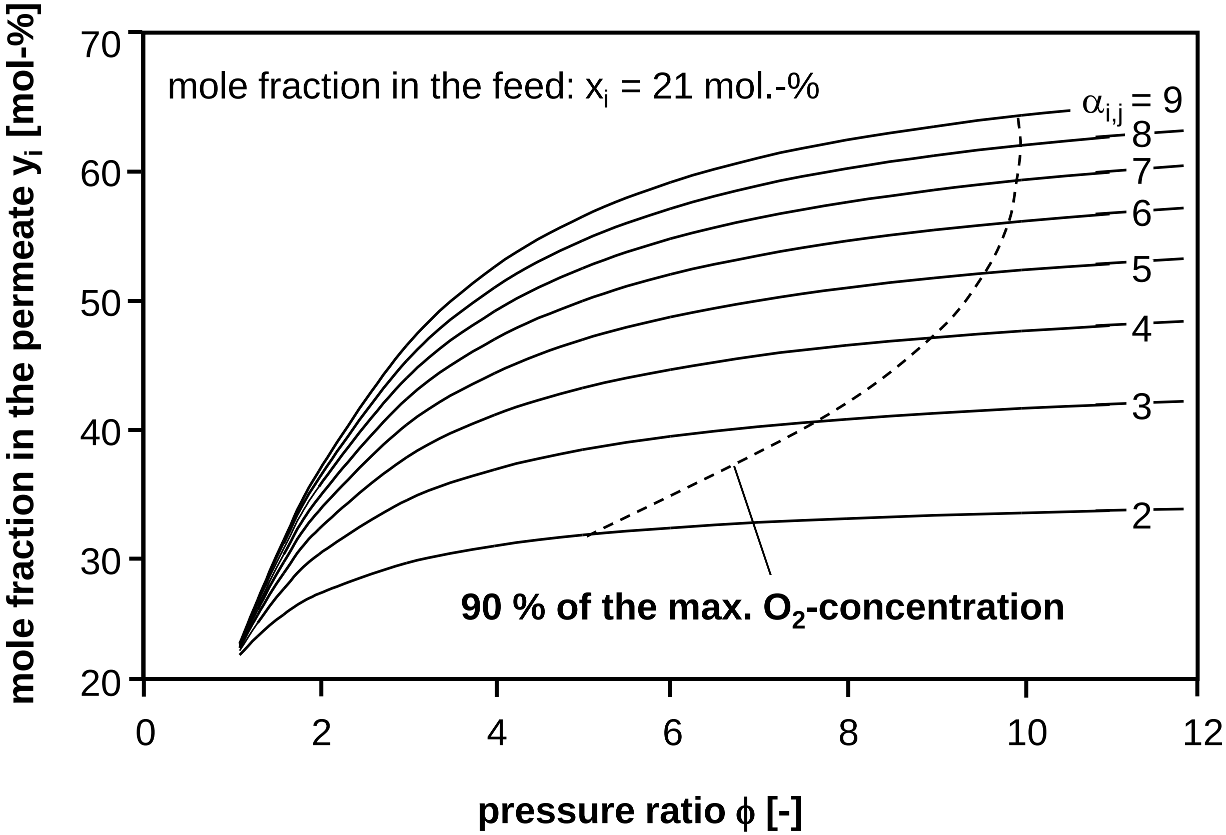
$$\phi \rightarrow \infty: \quad y_i = \frac{\alpha \cdot x_i}{(1 - x_i + \alpha \cdot x_i)}$$

infinite selectivity



$$\alpha \rightarrow \infty: \quad y_i = \phi \cdot x_i$$

Binary mixtures - ϕ und α



- Rule of thumb for optimized operation: $\phi \approx \alpha$

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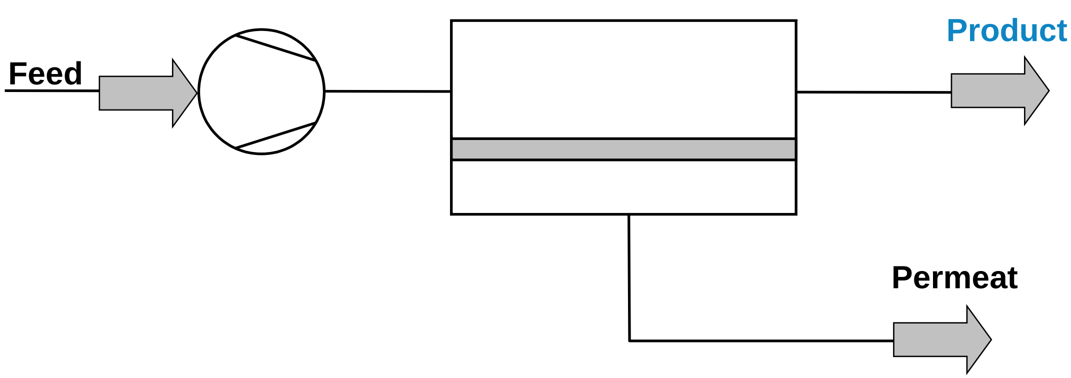
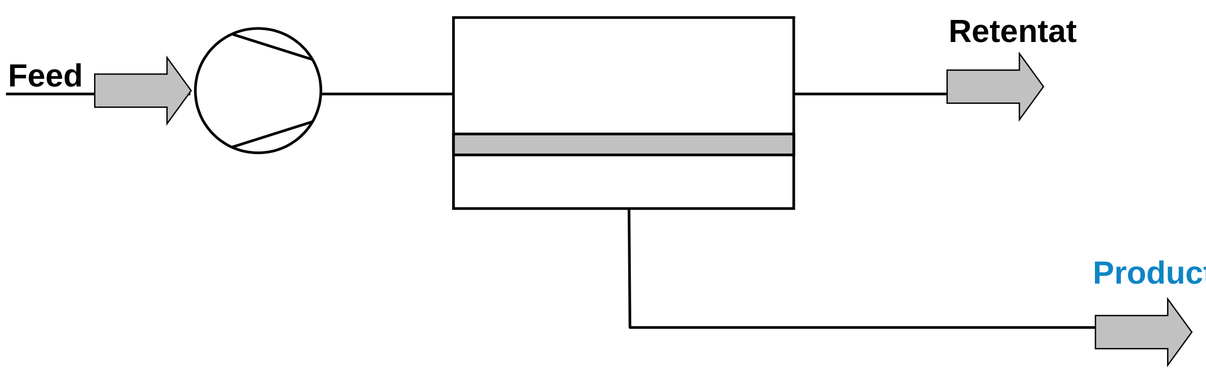
Product in the retentate

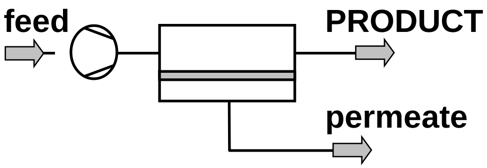


Product in the permeate



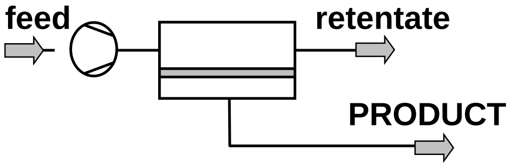
Good to know...

- Is the product in the retentate...
  ...any purity x_{Ret} can be achieved with a single stage unit!



  However...
  - Risk of poor product recovery $\eta = \dot{n}_{i,Ret} / \dot{n}_{i,Feed}$
    $A_{mem} \rightarrow \infty$ ➔ product stream $\rightarrow 0$ ➔ recovery $\eta \rightarrow 0$

- Is the product in the permeate...
  ....purity y is limited by a and ϕ !
  - for high purity y, normally multi-stage operations are required
  - increased system complexity and energy demand → high costs



Multicomponent mixtures

- No analytical solution possible → iterative solution

$$1-\sum_{i=1}^{n} y_i = 0 \qquad \text{with} \qquad y_i = \frac{x_i y_1 \dfrac{Q_i}{Q_1}}{x_1 - y_1 \dfrac{p_p}{p_f}\left(1-\dfrac{Q_i}{Q_1}\right)}$$

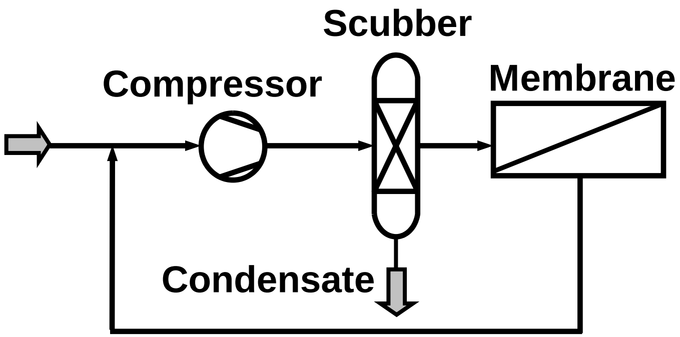
- Simplification by a quasi-binary mixture:
  fast/slowly permeating species are summarized in groups

average permeabilities: $\overline{Q_{12}} = \dfrac{x_1 Q_1 + x_2 Q_2}{x_1 + x_2}$ $\qquad \overline{Q_{34}} = \dfrac{x_3 Q_3 + x_4 Q_4}{x_3 + x_4}$

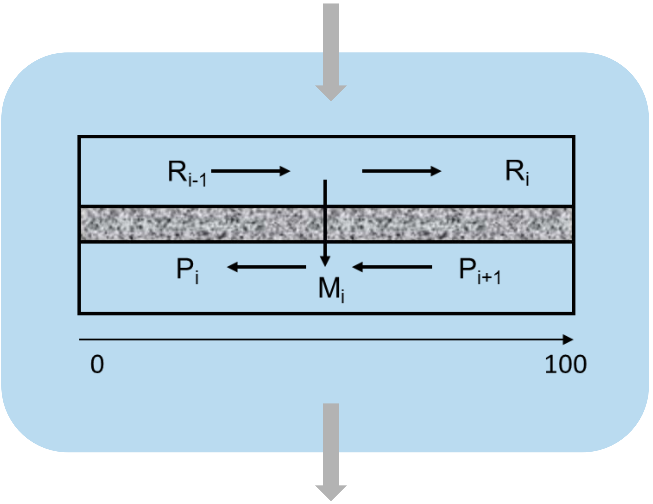
for $\quad Q_1 > Q_2 >> Q_3 > Q_4$

Plant design

Complete process-modelling (e.g. AspenPlus®, Pro2, etc.)



„Stand-alone“-calculation of module performance (e.g. Fortran, C++, Matlab, etc.)



Model for local mass transport

Module design - possible tasks

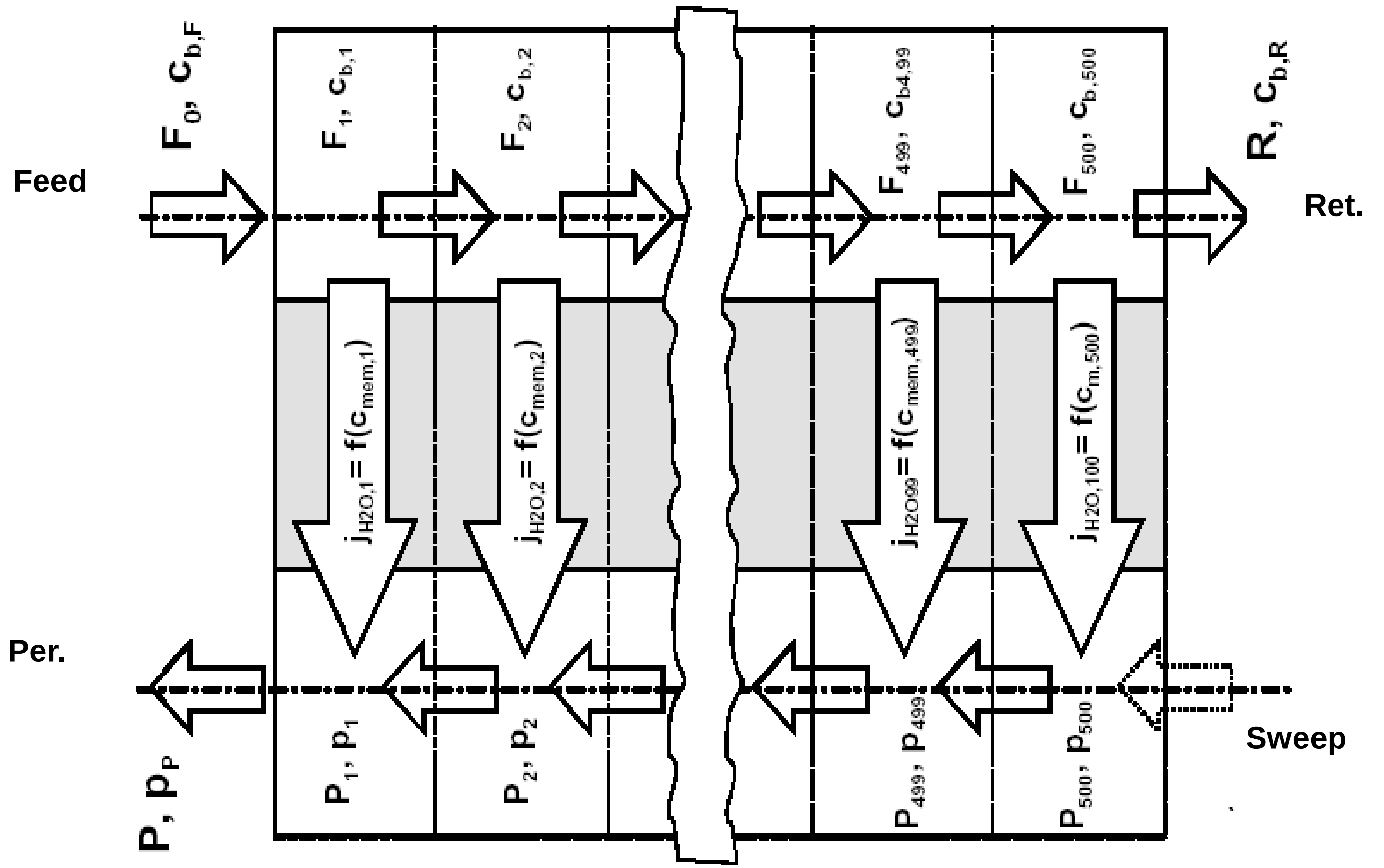
- Designing a module for given process specifications

or

- Calculating the product composition and recovery for a given module

Solution 1 - numerical

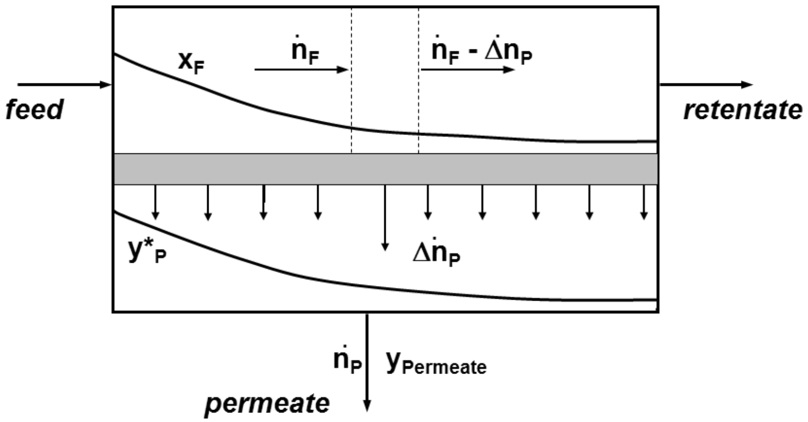
- Numerical solution of differential equations (1D, 2D, 3D)



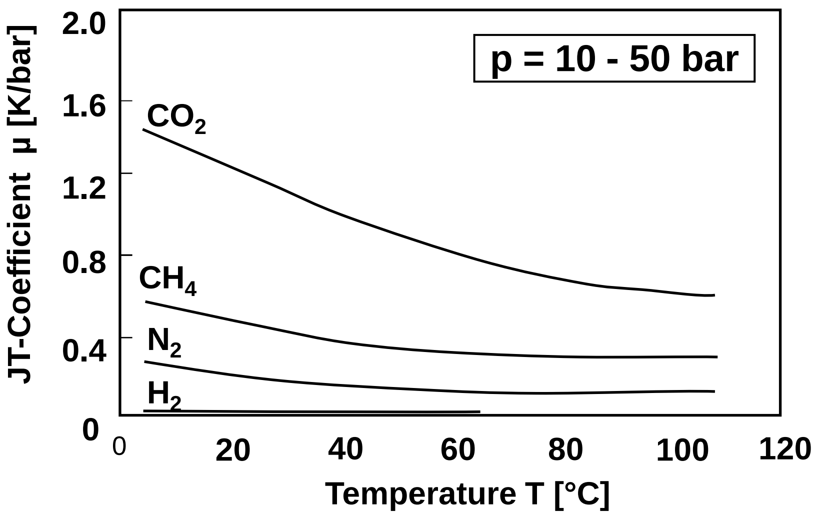
Solution 1 - numerical

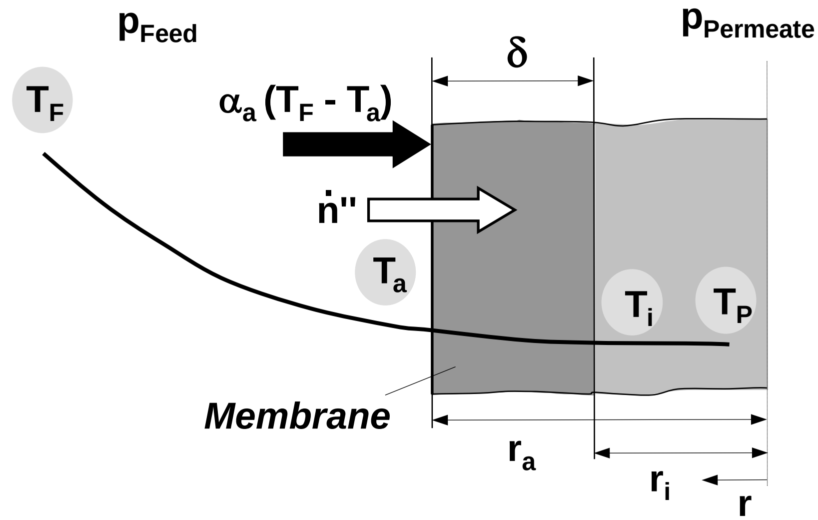
- Information required
  - local mass transfer: permeances $Q_i(T)$ for each species
  - flow pattern: co-/counter-current, unhindered permeate
  - geometry: feed/permeate channel dimensions

- Encountered difficulties:
  - multi-component mixtures
  - non-linear concentration/temperature profiles along the membrane
  - „non-idealities"
    - polarization effects
    - pressure loss
    - real gas behavior
    - Joule-Thomson effect etc.



Joule-Thomson effect



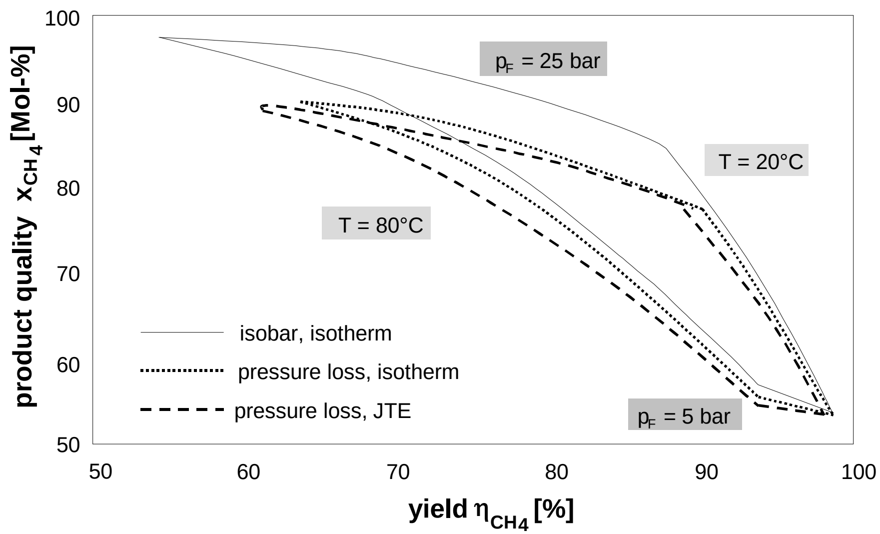


- thermodynamically: permeation = adiabatic expansion
- JT occurs at high Δp for real gases (JT-coefficients significantly above 0)

locally T↓ => membrane orthogonal T-profile
=> membrane axial T-profile
=> P↓, condensation (stability↓, selectivity↓)

Joule-Thomson effect

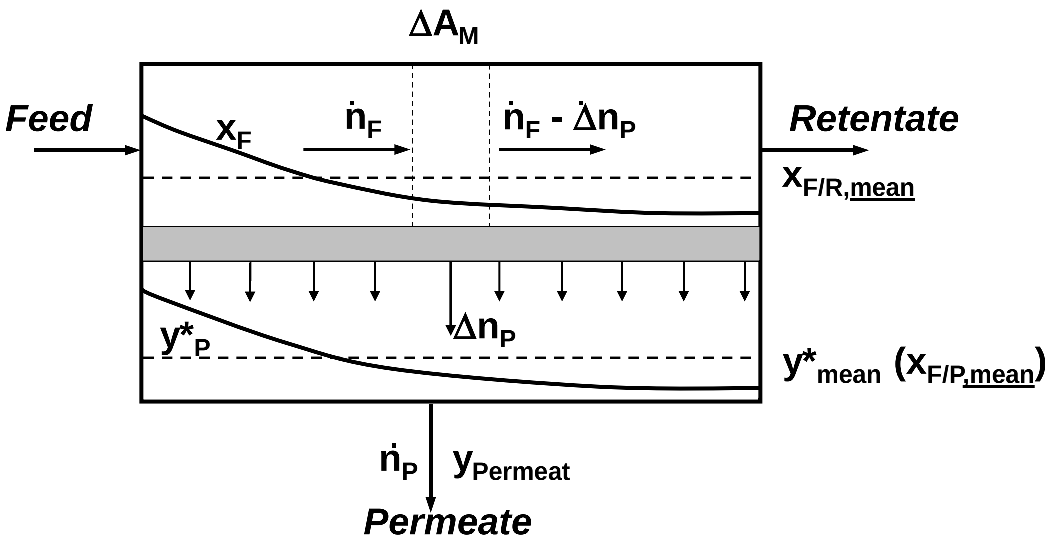
- JT shows in most cases a lower influence on the separation efficiency than calculating with the right pressure losses.



- JT should be considered, when dealing with...
  - high feed pressures and real gases (e.g. CO_2)
  - vapors in the feed close to condensation level

Solution 2 - mean-values

- Simplified mean-value method



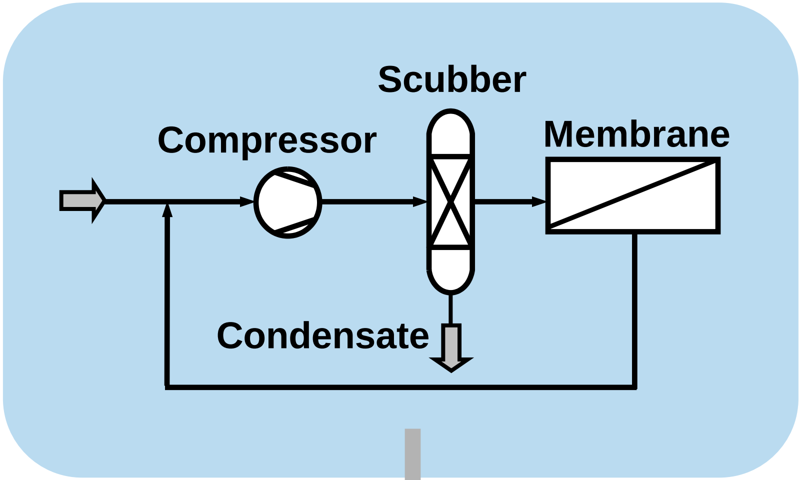
calculation of mole fractions with mean values

$y_{mean}=f(x_{f/r,mean}, \Phi, \alpha)$

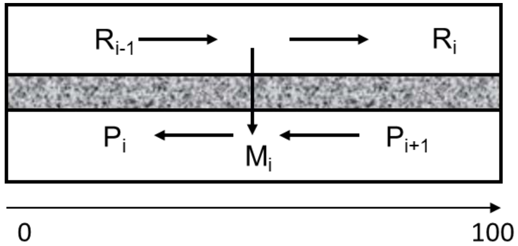
➡ Rough estimation of A_{mem} becomes possible.

Plant design

Complete process-modelling (e.g. AspenPlus®, Pro2, etc.)



„Stand-alone"-calculation of module performance (e.g. Fortran, C++, Matlab, etc.)



Model for local mass transport

Overview

- Materials & separation mechanisms
- Parameters describing the transport properties
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  - N_2 from ambient air
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The GP-market

GP- market	membrane market (US$ million) 2000	2010	2020
• N_2 from air	75	100	125
• O_2 from air	<1	10	30
• H_2-separation	25	60	100
• natural gas	30	90	220
• vapor/N_2	10	30	60
• vapor/vapor	0	30	125
• other	10	30	100
total	150	350	760 [8]

- 90% of the market
  - implies applications around permanent gases:
    N_2/O_2-separation, CO_2/CH_4-separation, H_2-separation from nitrogen, argon or methane
  - is dominated by 8 polymer materials

- Companies: Air Products, Air Liquide, Parker, Praxair, Kvaerner, UOP (Honeywell), UBE, MTR, Cynara (NatcoGroup), GKSS licencees

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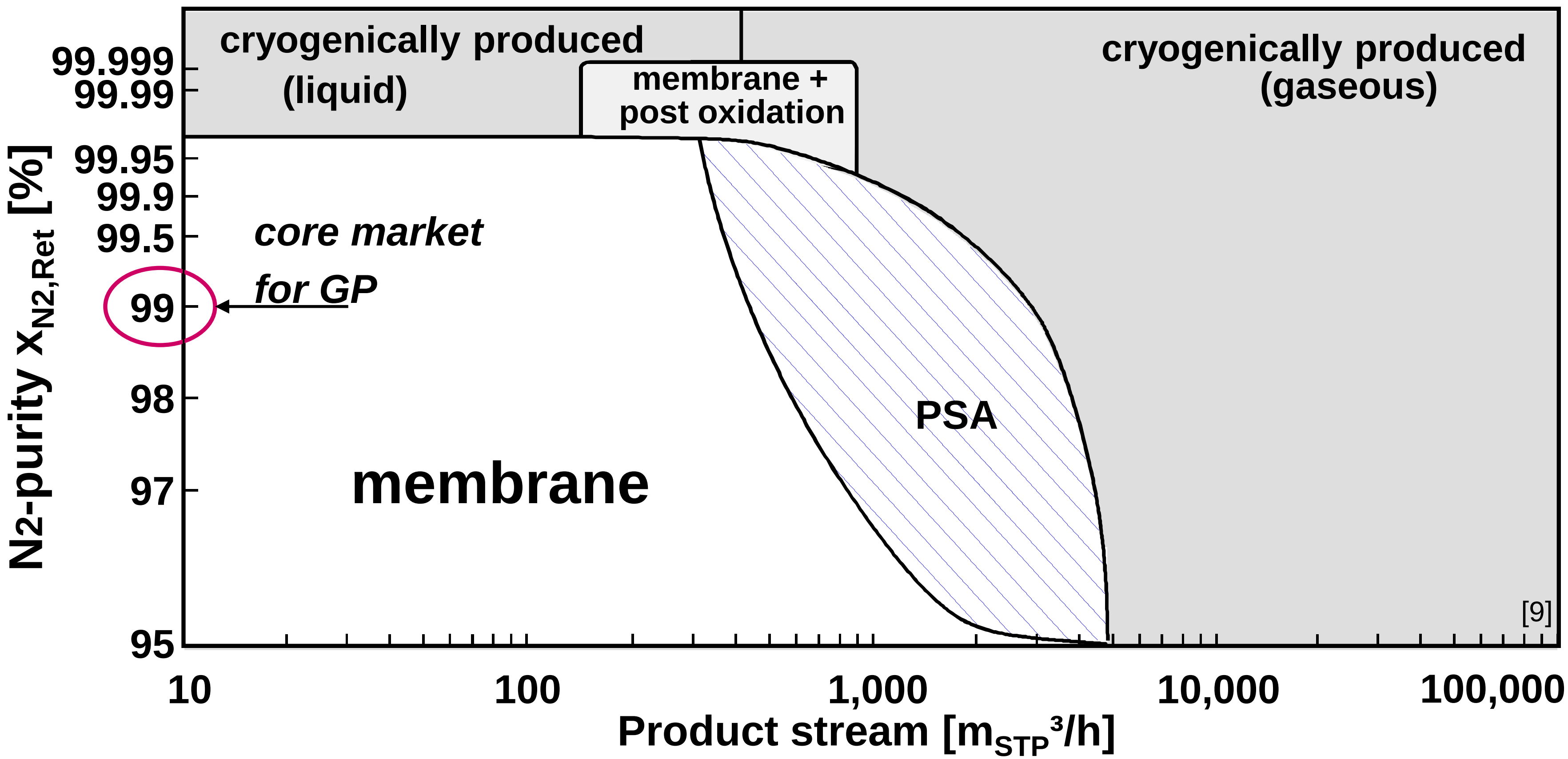
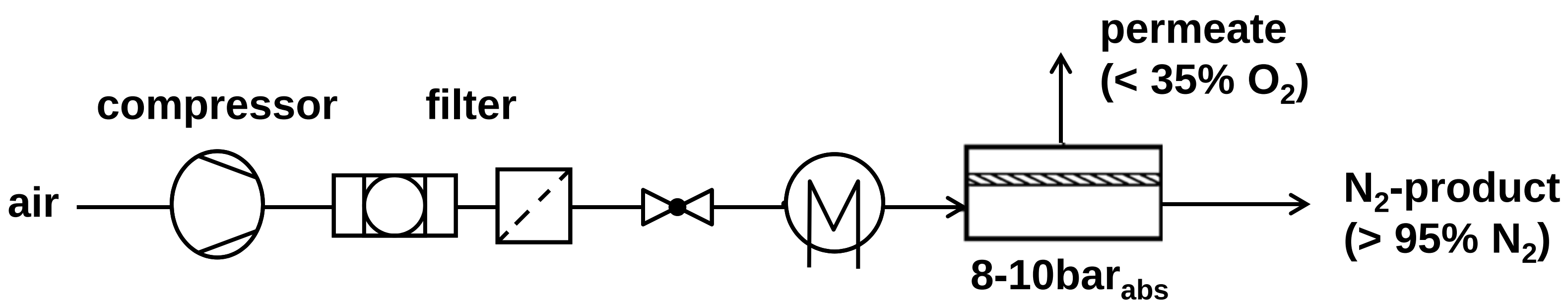
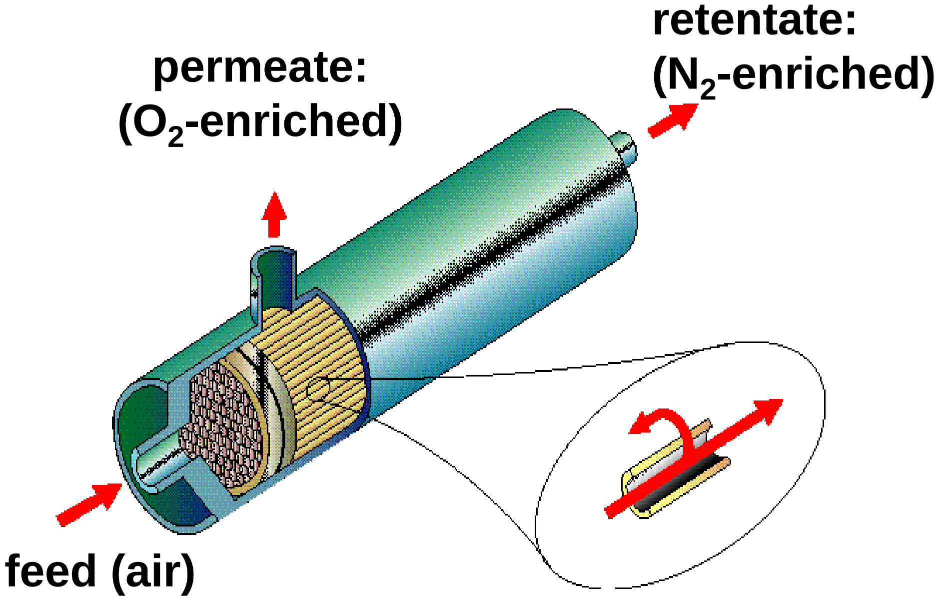
N_2-separation - state of the art



GP is the process of choice for moderate purities and small to intermediate product stream

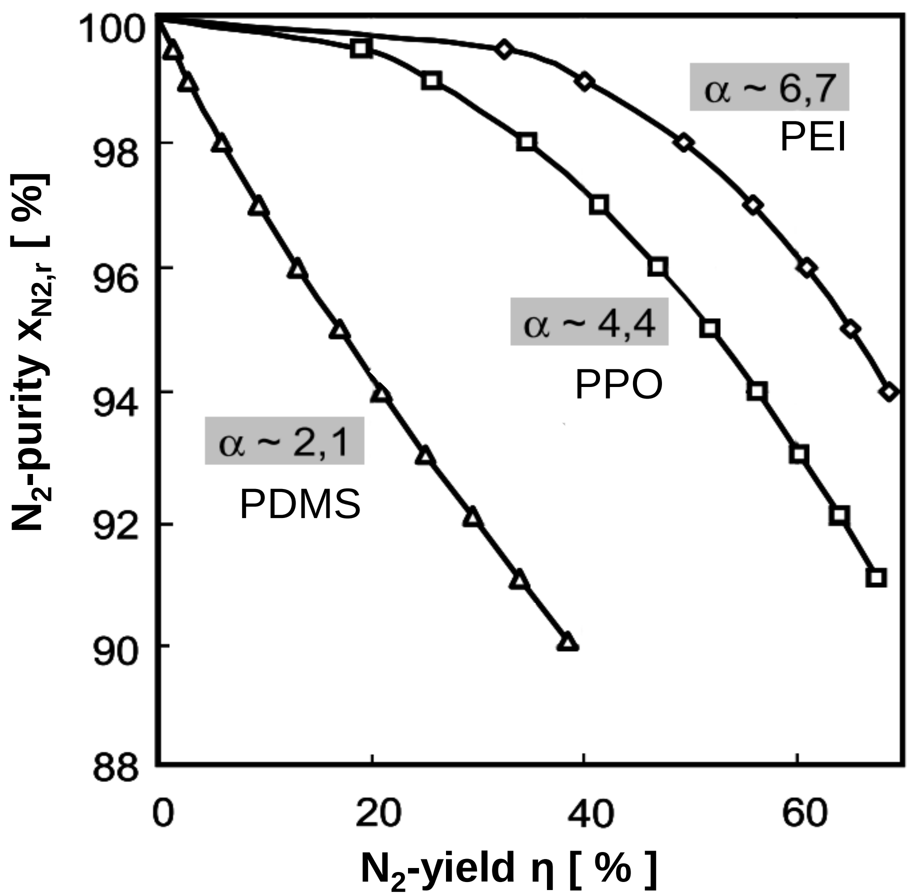
Process scheme





Separation performance: $x_{N2}(\eta)$

- **N_2-purity** in the retentate $x_{N2,r}$ can be determined as a function of **N_2-yield** η :
  - $x_{N2,r} = f(\eta, x_f, \alpha, \phi, A)$



$$\eta = \frac{x_r \dot{n}_r}{x_f \dot{n}_f}$$

N_2-enrichment - good to know...

- GP economical for small/intermediate product streams and moderate purities (90...99 %)

- Product is in the retentate: any purity within a single stage
  - $\eta\downarrow$ with low α
  - highly selective membranes:
    - $\eta\uparrow \rightarrow$ energy demand ($P_{compressor}$) $\downarrow$
    - $Q\downarrow \rightarrow A_{mem}\uparrow$

- investment costs:
  - membrane modules < 20 %
  - compressor ≈70 %

⇨ for every membrane material, there is an optimal pressure ratio minimizing energy and membrane area

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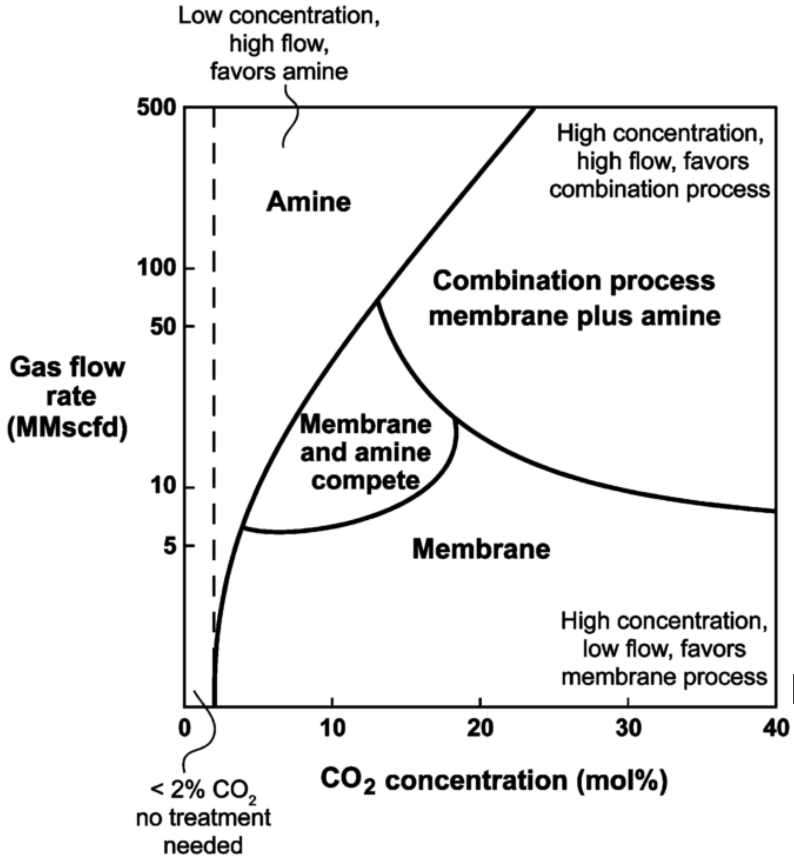
CO_2-depletion of natural gas



[5]

- membranes: CA, PI (glassy polmers with selectivities of 10-20)
- p_{feed}: 30-60bar
- modules: hollow fibres/spiral wound modules

CO_2-depletion of NG - system design

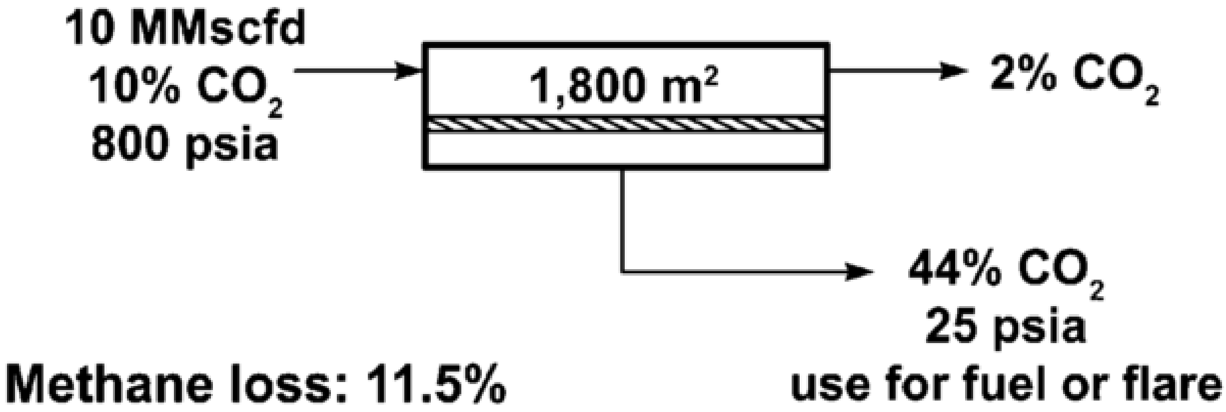
- Selection criterias:
  - selectivities and permeances of the membranes
  - CO_2 concentration of the gas and the separation required
  - value of the gas
  - location of the plant (offshore/onshore)

capacity: 10000m³/h, depletion of 6% CO_2 in the feed to pipelinestandard of 2%

CO_2-depletion of NG - system design

- Single stage plant

1 MMscfd = 1180m^3/h
1 psia = 0.06895bar



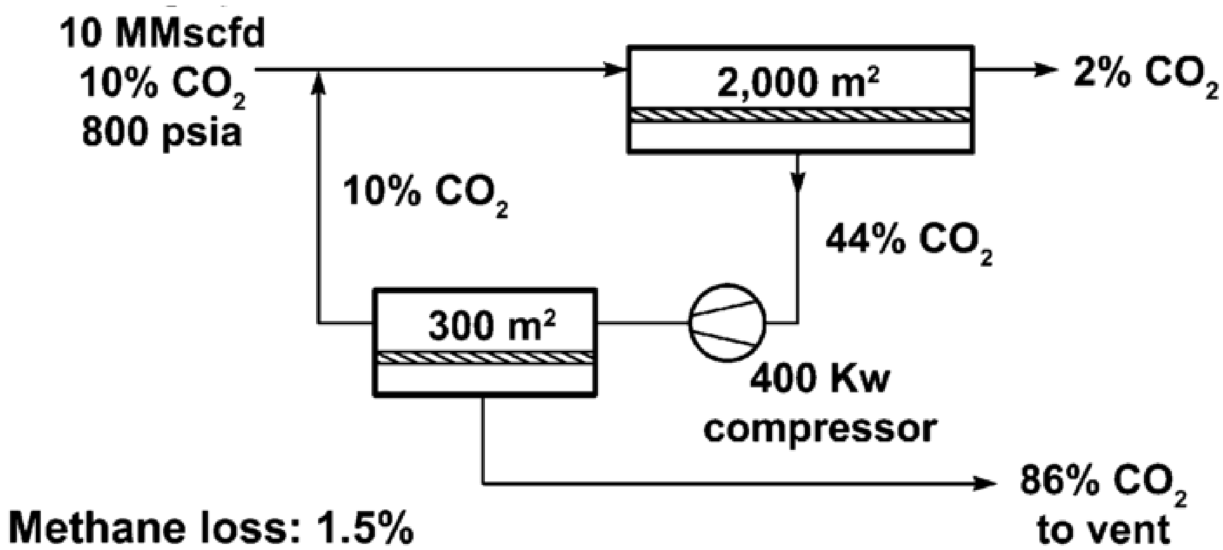
[5]

for very small gas flows (<1MMscfd)
+ no rotating parts
- loss of methane

CO_2-depletion of NG - system design

- Multi stage plant

1 MMscfd = 1180m³/h
1 psia = 0.06895bar



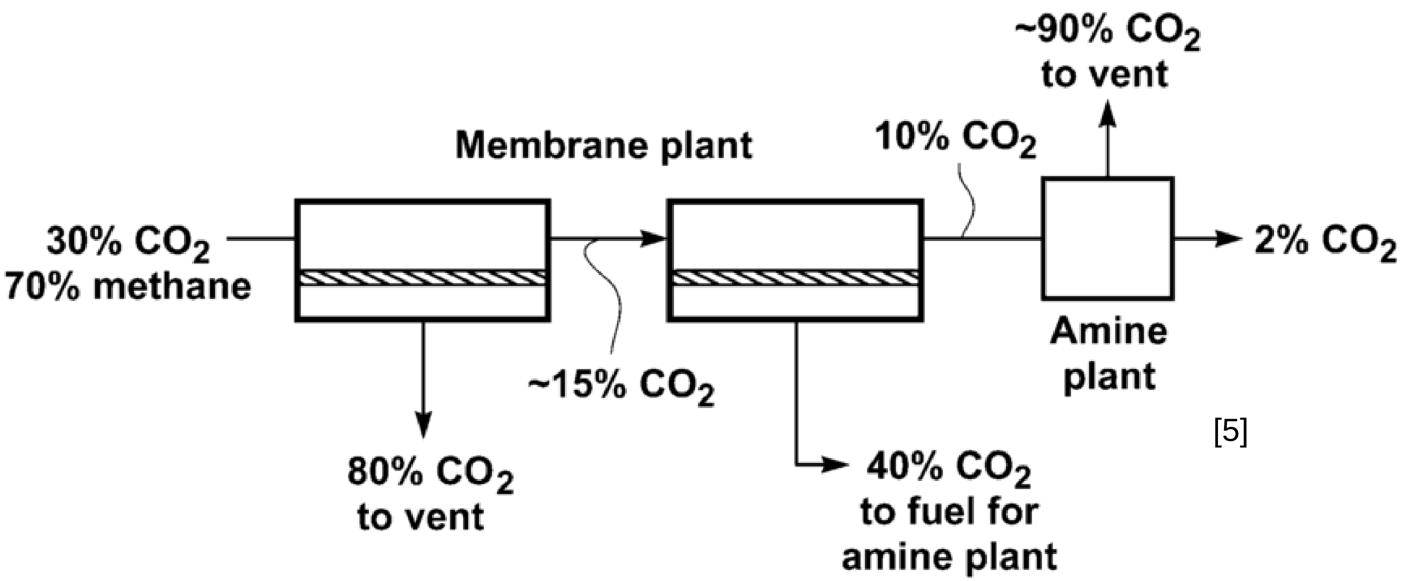
[5]

higher gas flows
- increased capital costs
+ more economic

CO_2-depletion of NG - hybrid process

- Hybrid plant

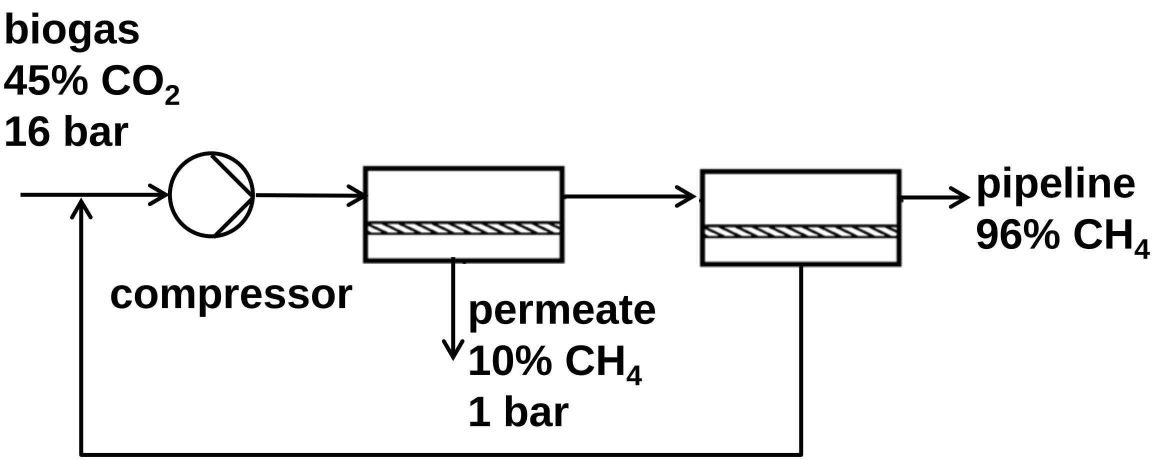
1 MMscfd = 1180m^3/h
1 psia = 0.06895bar



[5]

- offers a low cost alternative to all-amine / all-membrane systems
- higher complexity → limited to large plants

CO_2-depletion of biogas



[10]

- landfill gas or sewage gas:
  usually 2-stage process (permeat of 2nd stage flowing back to global feed)
- membranes: polyimide/ polyaramide, (CO_2/CH_4-selectivity around 20-25)
- p_{feed}: 16-20bar
- methane losses ~ 10 %

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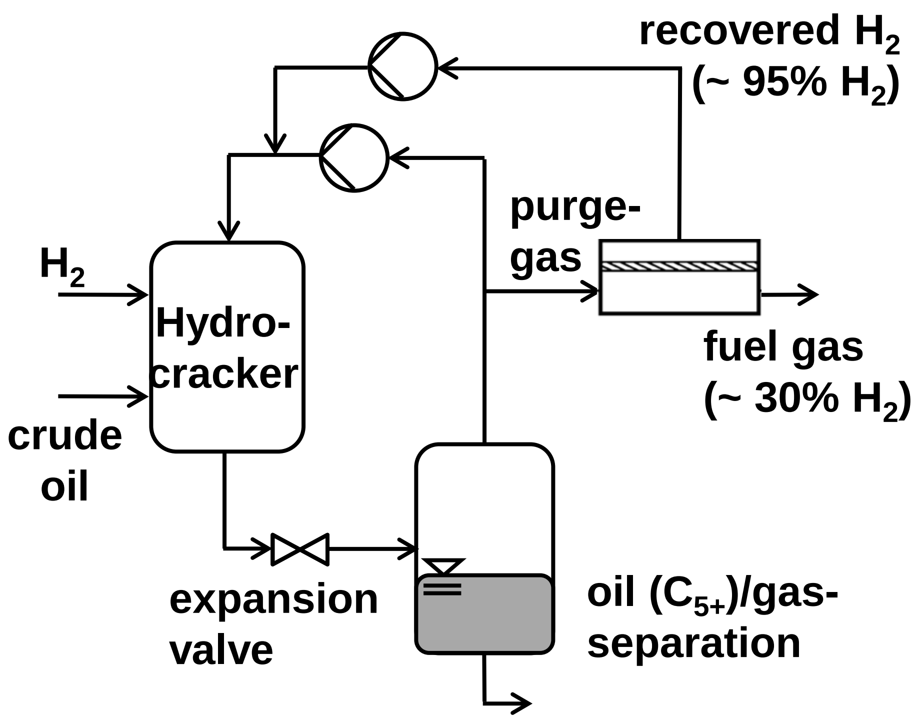
H_2-Recovery in refineries



- **without membrane:**

  non-reacted H_2 in purge gas is "lost" (post-combusted)

- **with membrane:**

  H_2 in purge gas is recirculated.

- crude oil-intermediates are contacted with H_2 for cracking (formation of C_{5+} favored)
- methane, ethane and propane are byproducts
- purge stream to prevent the accumulation of lighter hydrocarbons
- purge-gas composition: CH_4, ethane, propane and H_2 (75-80%)

H_2-Recovery in refineries

- Other applications of H_2-membrane plants:
  - synthesis gas treatment to adjust the H_2/CO ratio
    e.g. for methanol production and oxosynthesis
  - H_2-recovery from purge gases at ammonium- and methanol synthesis
  - H_2-recovery from PSA- or cracker-offgas

good to know...

- H_2 is 3 times as valulable recovered than burned
- worldwide, more than 100 H_2-membrane plants after hydrocrackers are installed.
- main problems:
  - membrane fouling due to condensed hydrocarbons
    → precaution measures: heating the feed stream (~ 80°C)

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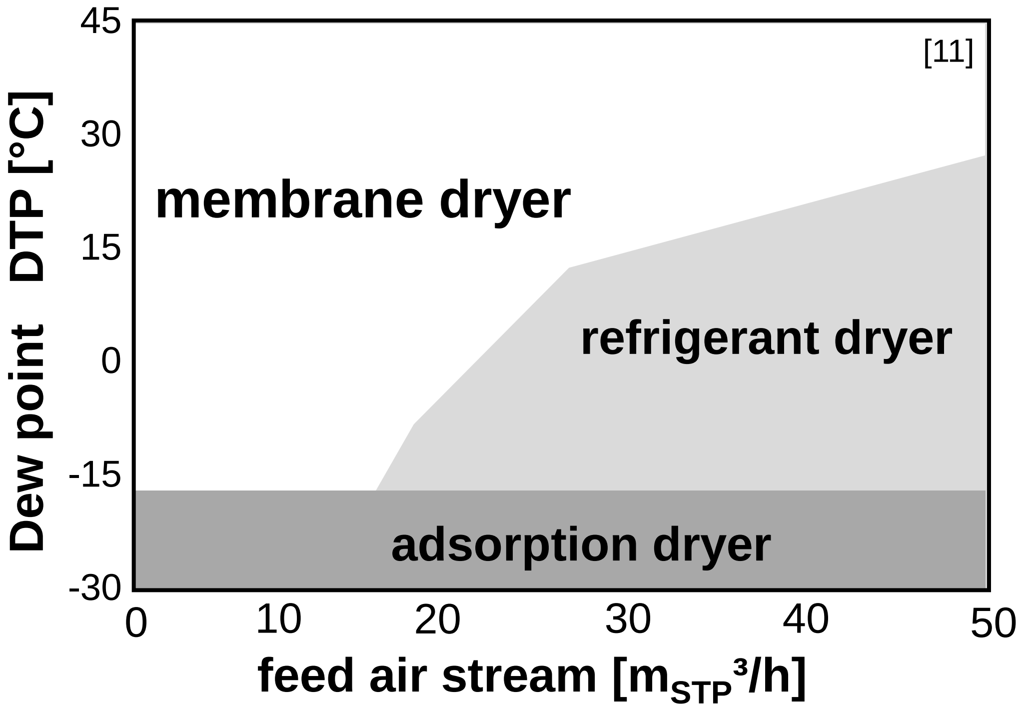
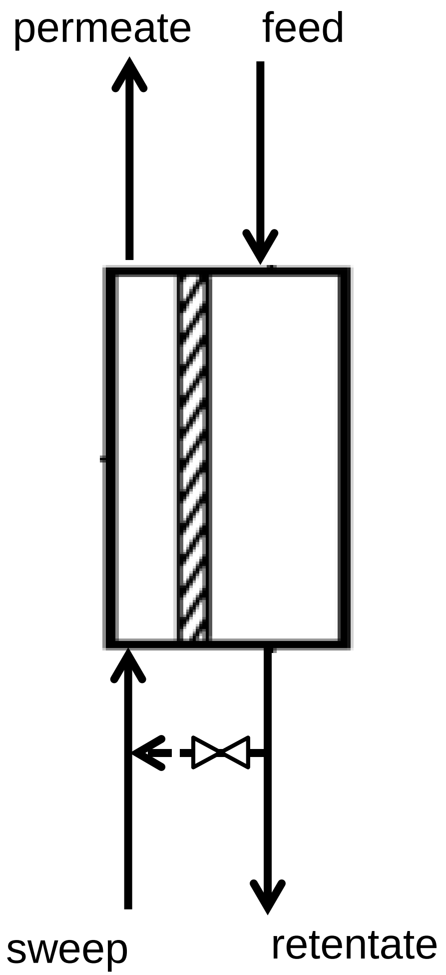
Pressured air dryer

- sweep gas use (partial retentate recirculation)
- easy and flexible installation
- especially drying to moderate DTP
- air losses: ~ 10 %





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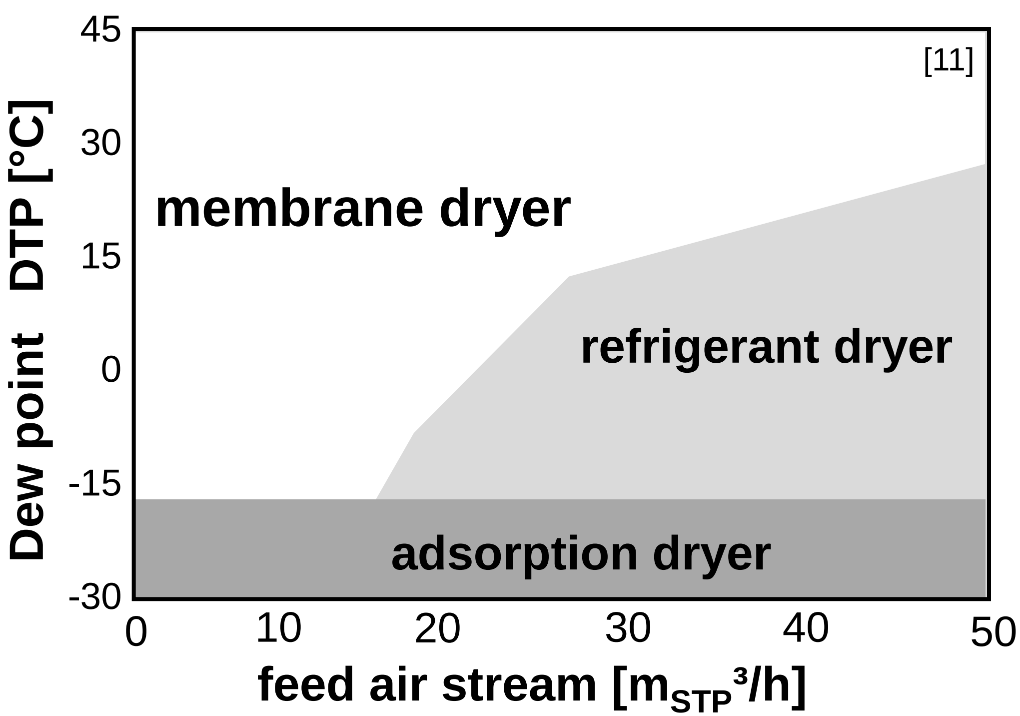

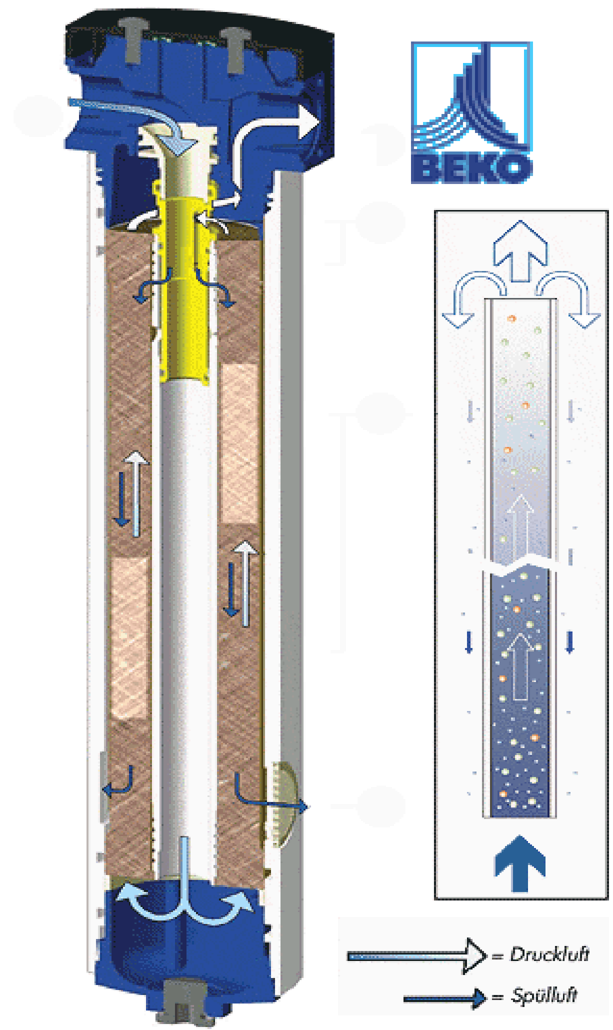

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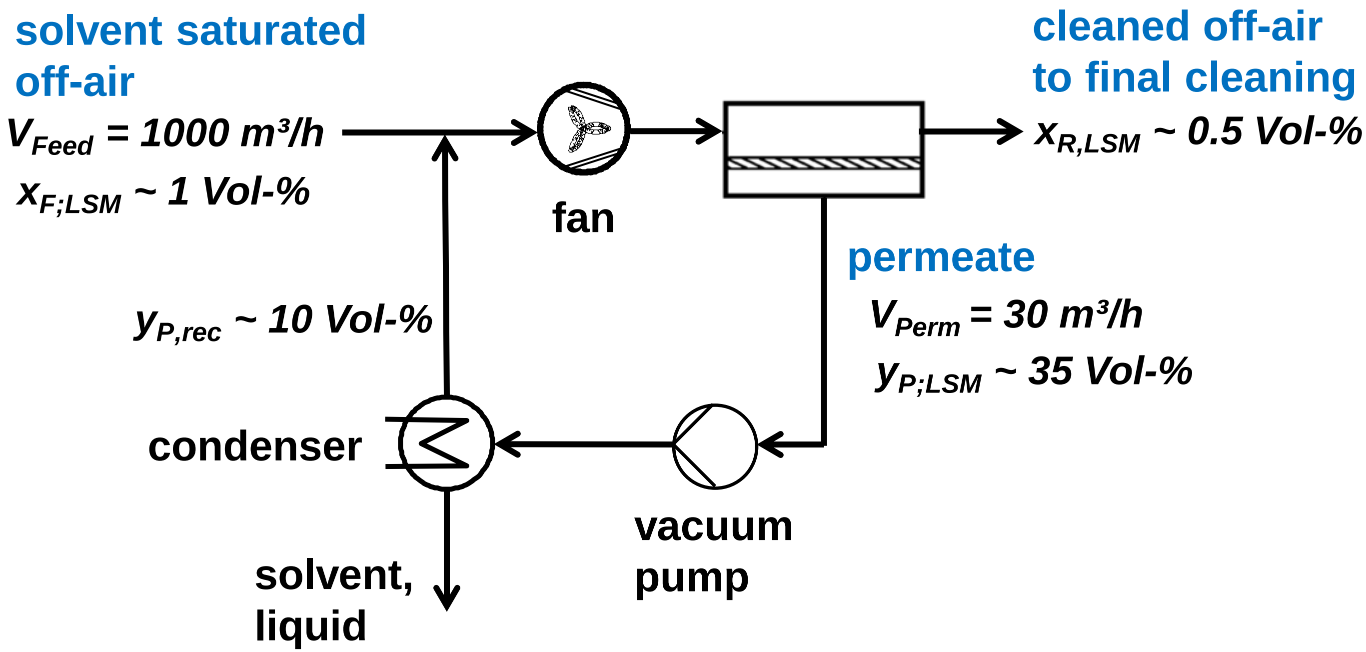
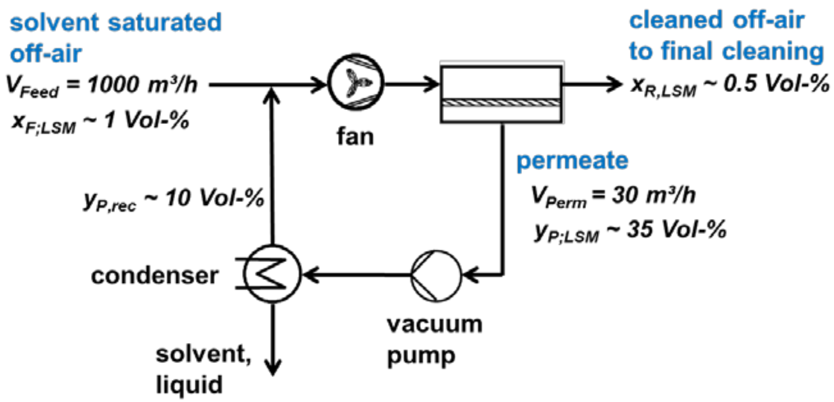
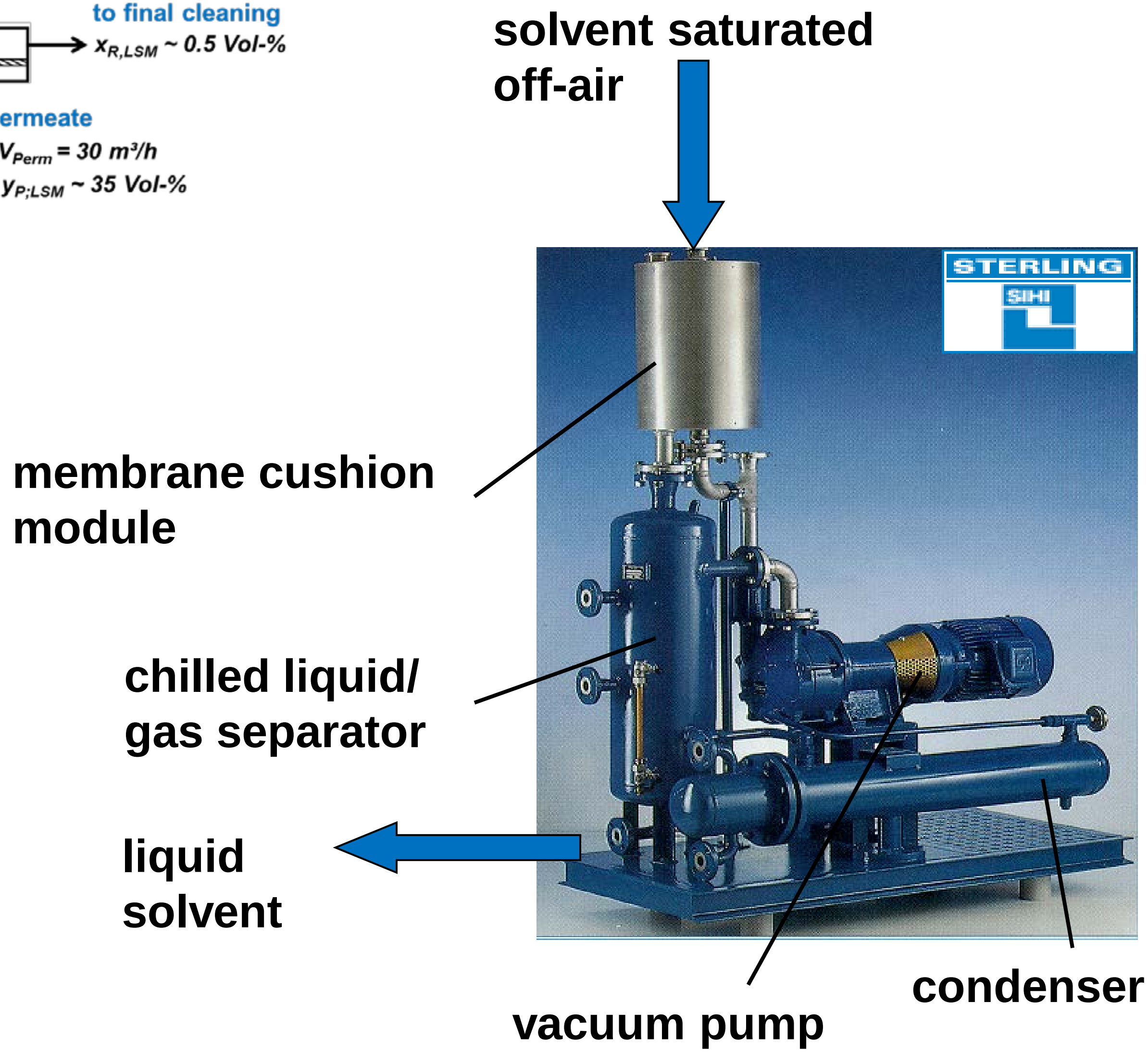
Solvent recovery from off-air (e.g. DMIA)



- membrane (PDMS) is highly selective for solvent
- strong solvent enrichment in permeate due to vacuum
- condensation is favoured by prior compression in vacuum pump

Solvent recovery from off-air





Solvent recovery - good to know...

- Profitable at
  - high solvent loads and moderate retentate purity
    (e.g. fuel vapour recovery)
  - low solvent loads only if solvent is expensive
    (recovery is driving factor, not air cleaning to legal levels)

- Air-cleaning down to "TA Luft" is possible but not profitable
  → post-processing (e.g. combustion, adsorption)

- Applications:
  propene/N_2, ethene/N_2, fuel vapors, cooling agents,
  solvents (hexane, acetone, toluene, etc.)

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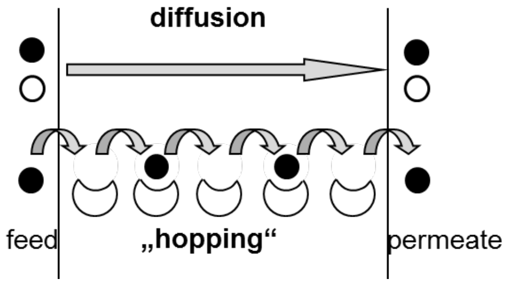
New membranes for future GP-modules

- ## Objectives:
  - membranes with better mechanical, thermal & chemical resistance
  - higher selectivities and permeabilities to overcome the upper bond (e.g. by species-specific (chemical) transport mechanism)

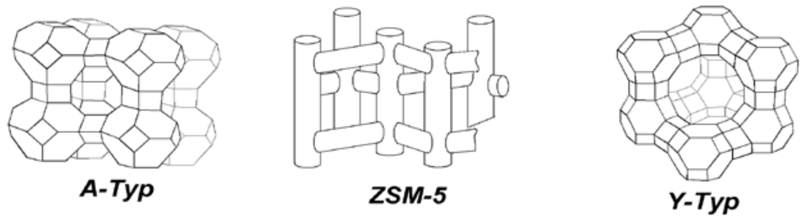
    common selectivities:
    $O_2/N_2 < 10$, $H_2/CO < 100$, H_2/N_2 100-200,
    $CO_2/CH_4 < 100$, $H_2O/air > 200$
  - as low-cost as nowadays polymer membranes



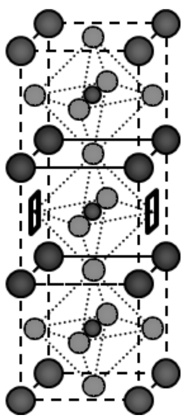
- ## Natural Gas treatment / CH_4 enrichment to pipeline quality
  - C_{3+} - separation
  - Water vapor separation
  - N_2 - separation

Alternative materials

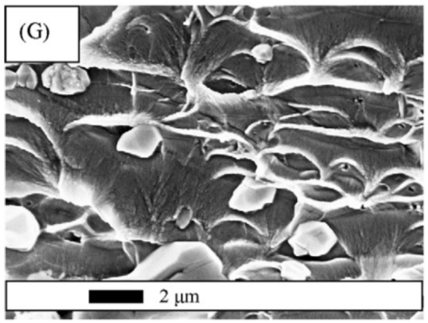
- porous materials?
  e.g. zeolites, carbon, glass, metal



- dense materials?
  e.g. metal membranes, perovskite



- mixed-matrix membranes?
  e.g. disperged particles in polymer matrix



[12]

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Conclusion

- Dense polymer membranes dominate the market
  - SDM describes the mass transfer
  - solubility/diffusivity selective materials
  - Robesons upper bond
  - influence of T, p, gas mixtures
- Modules/membranes:
  - permanent gases: hollow fibre / mainly glassy polymers
  - vapors: spiral wound or cushion modules / mainly rubbery polymers
- Theory of mass transport
  - limiting influence of α and ϕ

Conclusion

- Applications
  - N_2-enrichment, CO_2-depletion, H_2-recovery, air drying and solvent recovery
- Research is focusing on
  - membranes with higher selectivity and/or higher permeability, enhanced chemical resistance (especially in natural gas or refinery applications)
- Outlook
  - the GP-market is growing
  - with new materials further applications become more probable

Thank you for your attention

AVT.CVT - Chemical Process Engineering

Refernces

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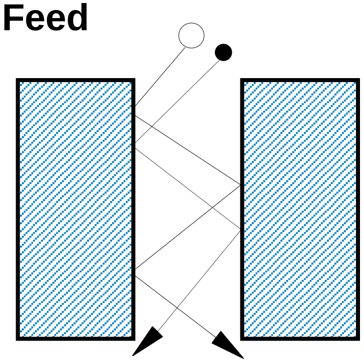
Separation mechanisms

Mesoporous Membrane

Feed



Permeate

d_P ~ 1 ... 20 nm

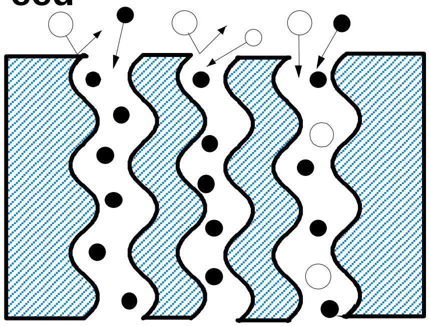
Knudsen diffusion

based on the dominance of gas/wall - collisions

inorganic

Microporous Membrane

Feed



Permeate

d_P ~ 0.3 ... 10 nm

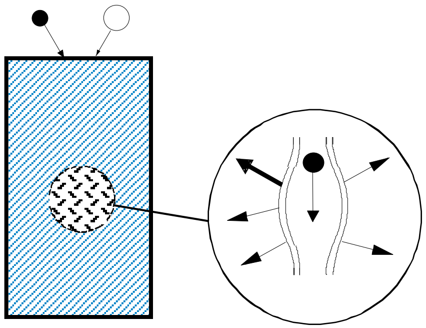
Molecular sieve separation

based on different diffusion rates of different molecules with different molecular sizes + adsorption effects

inorganic

Dense Membrane

Feed



Permeate

gaps in polymer matrix or free lattice site

Solution-Diffusion

based on different solubility- and diffusion coefficients

mainly polymers also inorganic

d_P > 20 nm: viscous flow without selectivity

Dense membranes

$$\dot{n}_k'' = -c_{km} b_{km} \frac{\partial \mu_{km}}{\partial z}$$ mit Nernst Einstein: $$D_{k0} = RT \cdot b_k$$

Beweglichkeit

Konzentration

$$\dot{n}_k'' = -c_{km} \frac{D_{km,0}}{RT} \frac{\partial \mu_{km}}{\partial z}$$ (Generalised Fick's Law of diffusion)

mit $\mu_i = \mu_i^0 + RT \ln a_i$ folgt $\dot{n}_k'' = -c_{km} D_{km,0} \frac{\partial \ln a_{km}}{\partial z}$

mit $c_{km} = S_k p_k$ folgt $\dot{n}_k'' = -S_k D_{km,0} \frac{d a_{km}}{dz}$

... leads with following assumptions...

1. non-coupled permeate fluxes
2. Henry's Law: $c_{km} = S_k\, p_k$
3. the chemical potential of each s at the membrane surface corresponding gas phase

...to a linear mass transport equation!

$$\boxed{\dot{n}_k'' = Q_i (p_{i,F} - p_{i,P}) = Q_i (x_i p_F - y_i p_P)}$$

Q_i: permeance
membrane and species specific

application specific