Gas Separations Using Polymer Membranes

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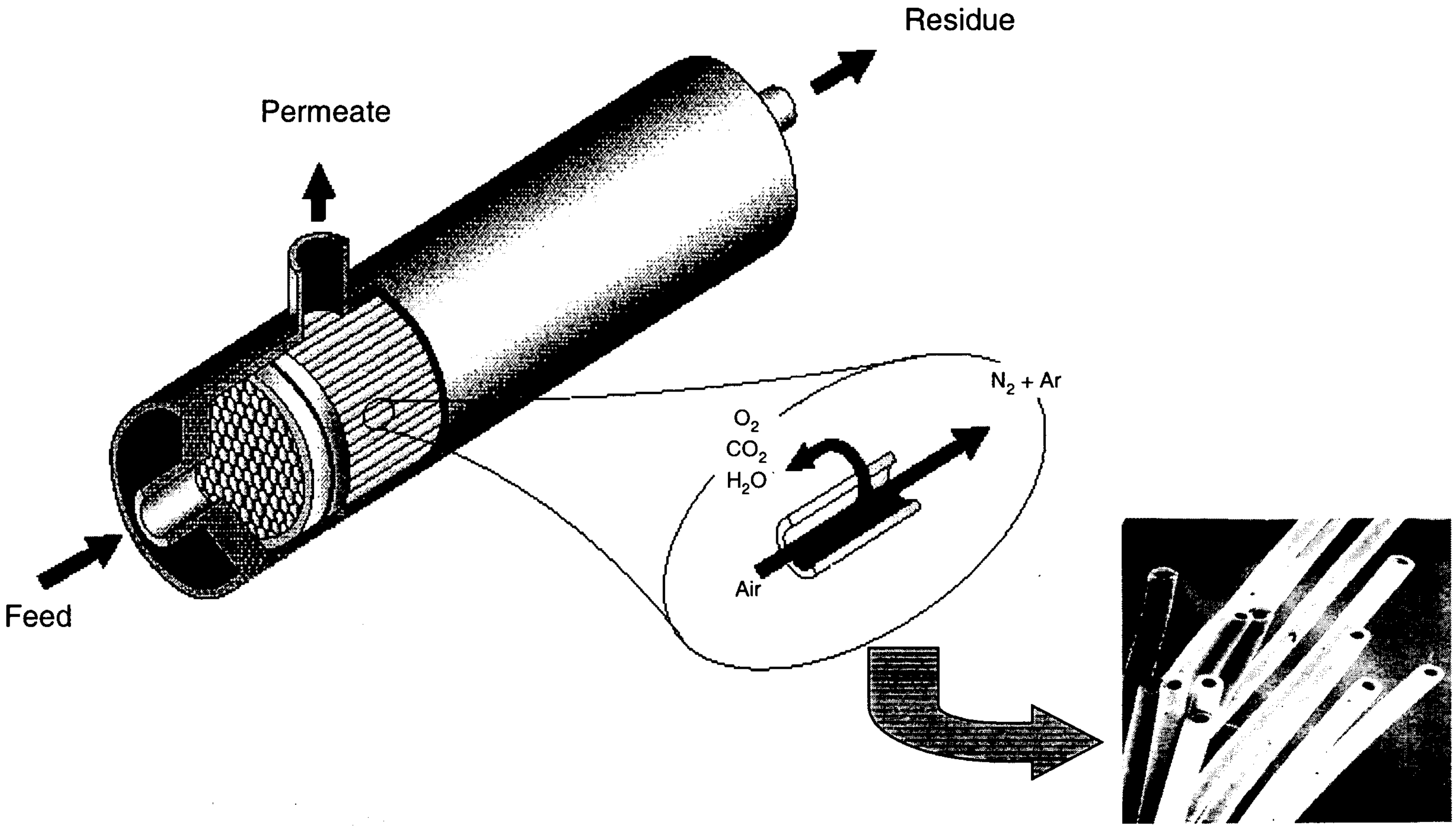
Hollow Fiber Membrane Contactor

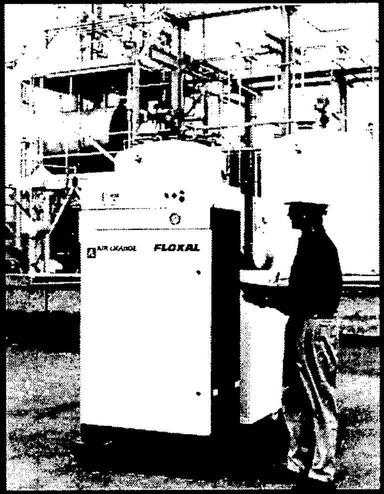


Key Issues in Gas Separation Using Polymer Membranes

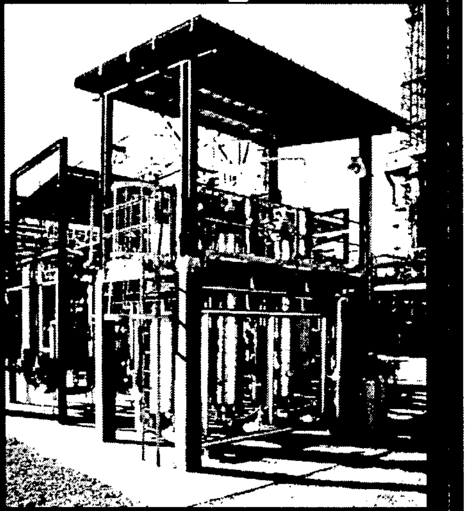
- Materials
  - High Permeability
  - High Selectivity
  - Stability in Process Environment
- Defect-Free, Thin, Selective Membranes
  - Asymmetric
  - Thin Film Composite
- Module/Process Engineering
  - Fluid Distribution in Module (Eliminate Bypassing, Dead Zones)
  - Module Connection Strategy (Series, Parallel, Both)
  - Other Engineering Issues (Pump vs. Vacuum, Process Integration, etc.)

Commercial Applications

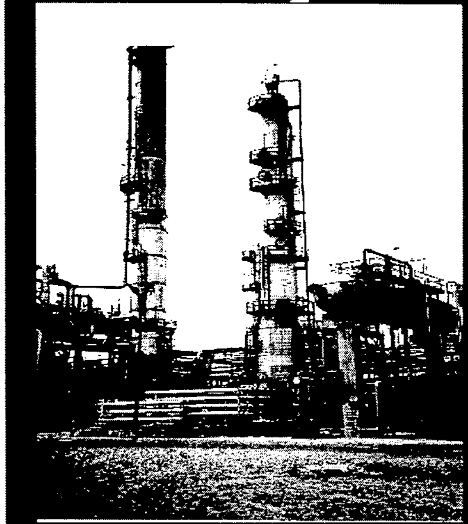
N_2



H_2



CO_2

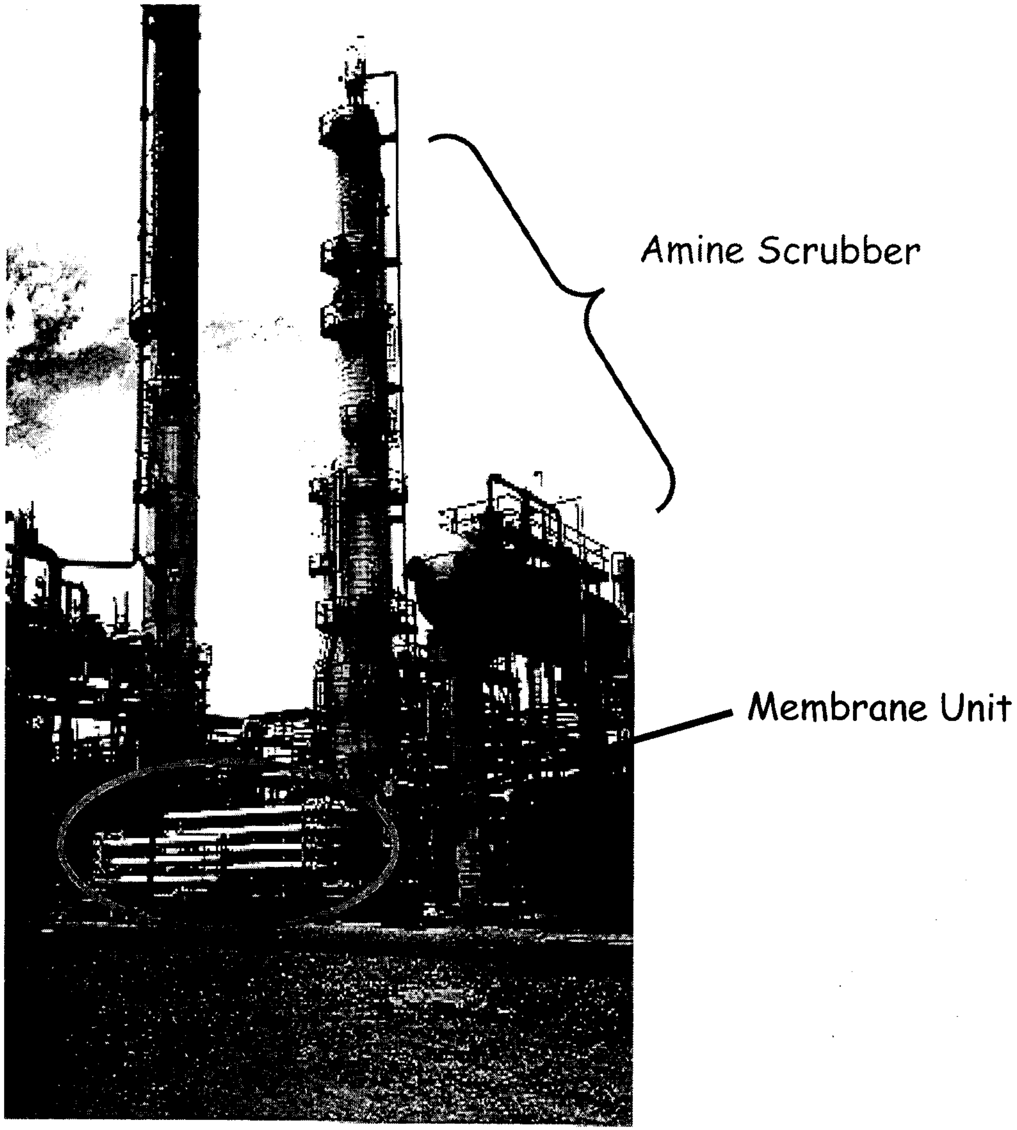


N_2 - Enriched Air
- Blanketing/packaging of food
- Aircraft fuel tank blanketing
- Underbalanced drilling
- Purging/transferring in CPI

H_2 Separation
- Syngas ratio adjustment
- H_2 removal from NH_3 purge
- H_2 recovery from HCs

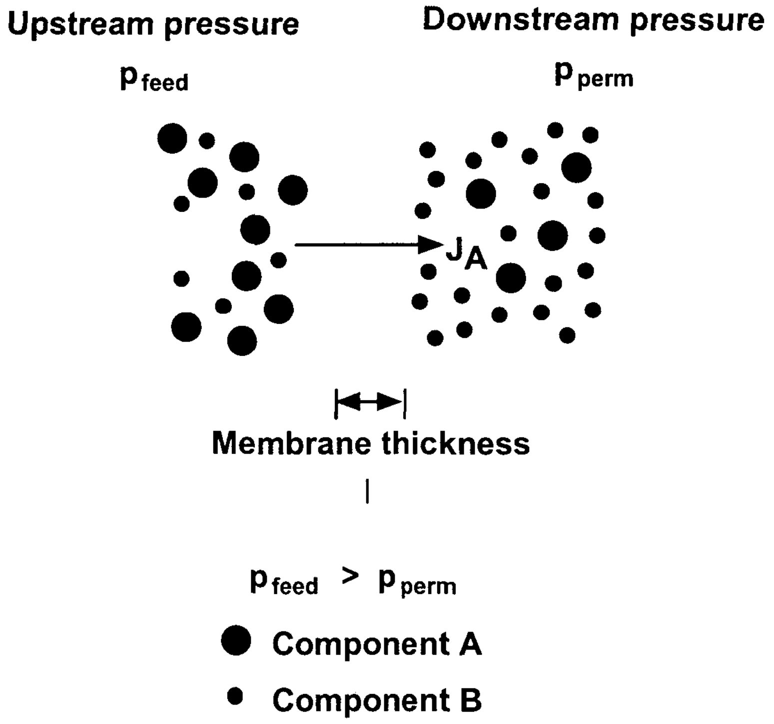
CO_2 Separation
- Natural gas sweetening

Advantages of Membranes



- Small footprint
- No moving parts
- Low energy

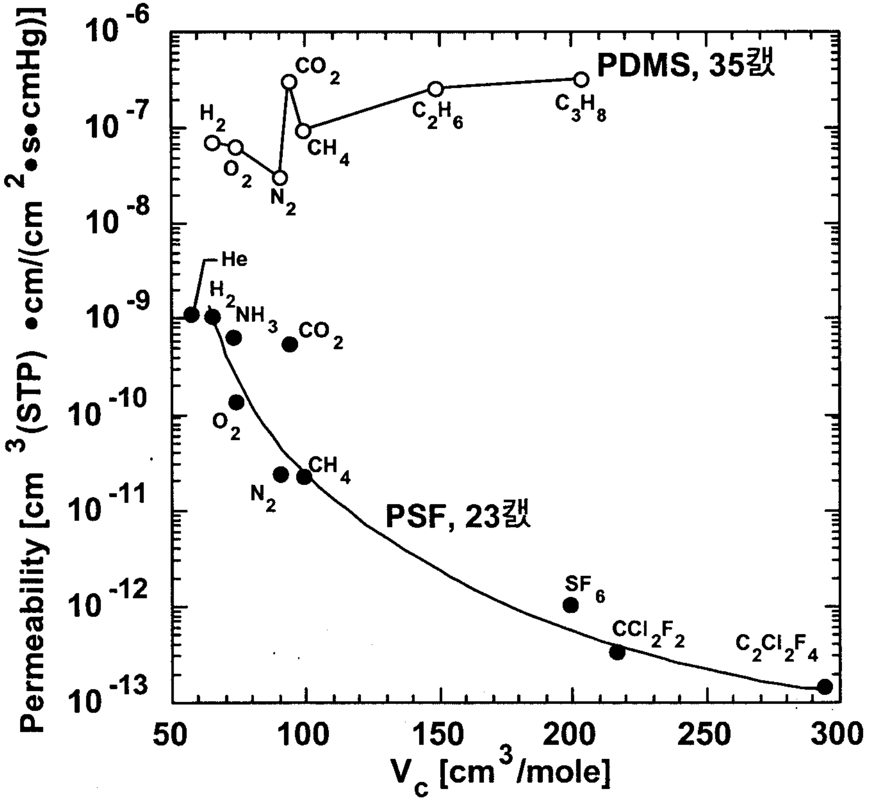
Gas Transport in Polymers: Solution-Diffusion Mechanism



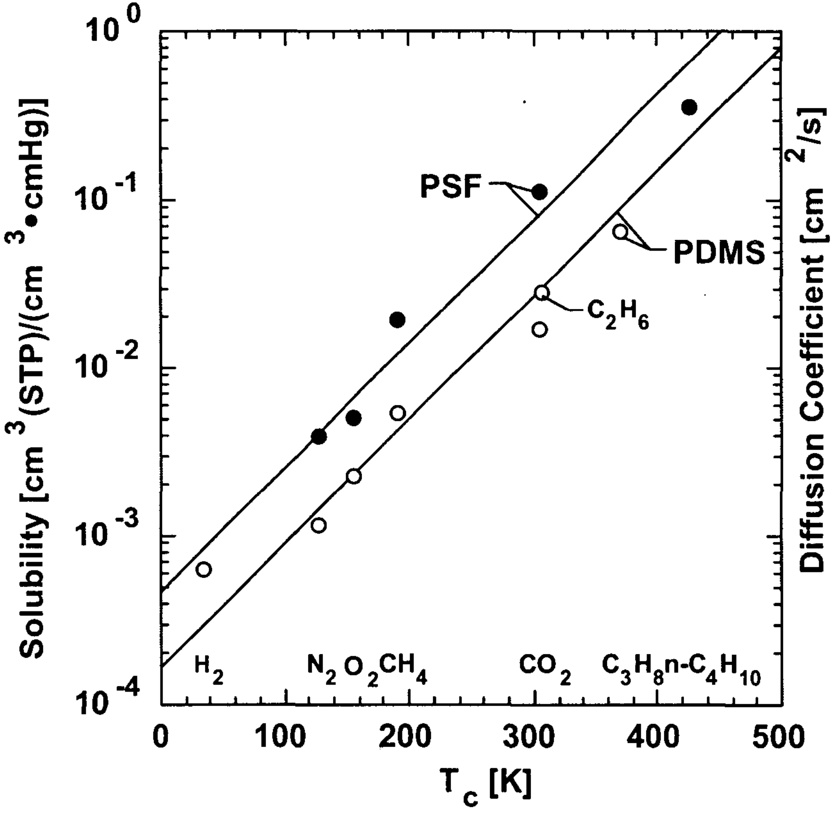
- Flux of A $\equiv J_A = \dfrac{P_A\,(p_{feed,A} - p_{perm,A})}{l}$
- Permeability of A $\equiv P_A = D_A\,S_A$,
  where $D_A \equiv$ Diffusion coefficient of A
  $S_A \equiv$ Solubility coefficient of A
- Selectivity $\equiv \alpha_{A/B} = \dfrac{P_A}{P_B} = \underbrace{\left(\dfrac{D_A}{D_B}\right)}_{\text{Mobility selectivity}}\underbrace{\left(\dfrac{S_A}{S_B}\right)}_{\text{Solubility selectivity}}$

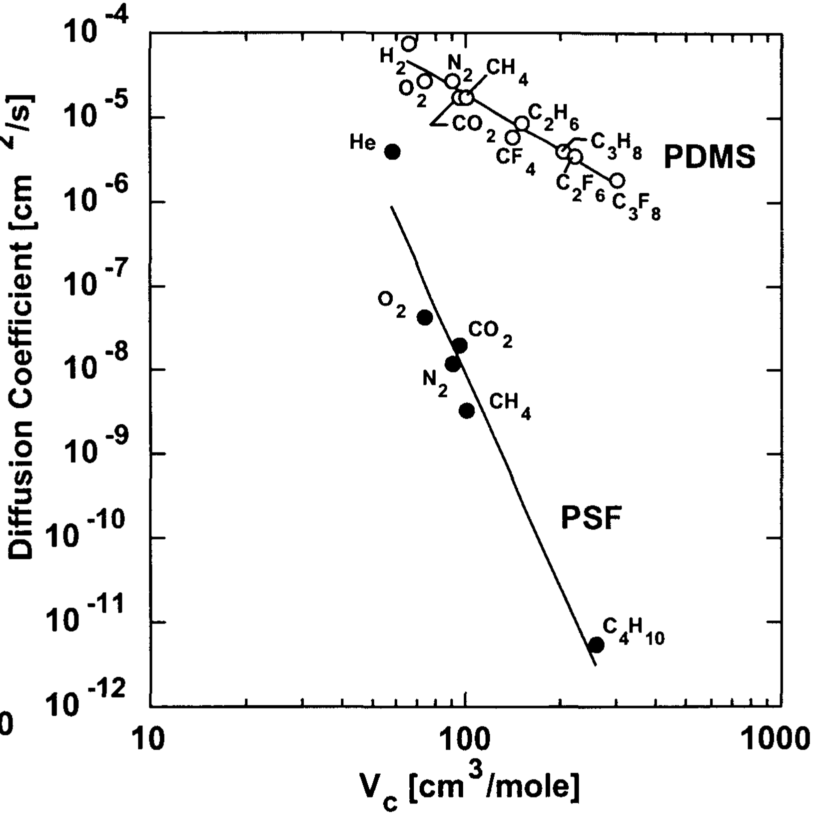
(1) *Sorption on upstream side*
(2) Diffusion down partial pressure gradient
(3) Desorption on downstream side

Gas Transport in Polymers:
Diffusivity-Selective & Solubility-Selective



Solubility & Diffusivity in Polymers:
Diffusivity-Selective & Solubility-Selective Materials





Gas Separation Based on High Diffusivity Selectivity: O_2/N_2, H_2/CO, H_2/HC, CO_2/CH_4

$$\alpha = \frac{P_{\text{Small}}}{P_{\text{Large}}} = \frac{D_{\text{Small}}}{D_{\text{Large}}} \frac{S_{\text{Small}}}{S_{\text{Large}}}$$

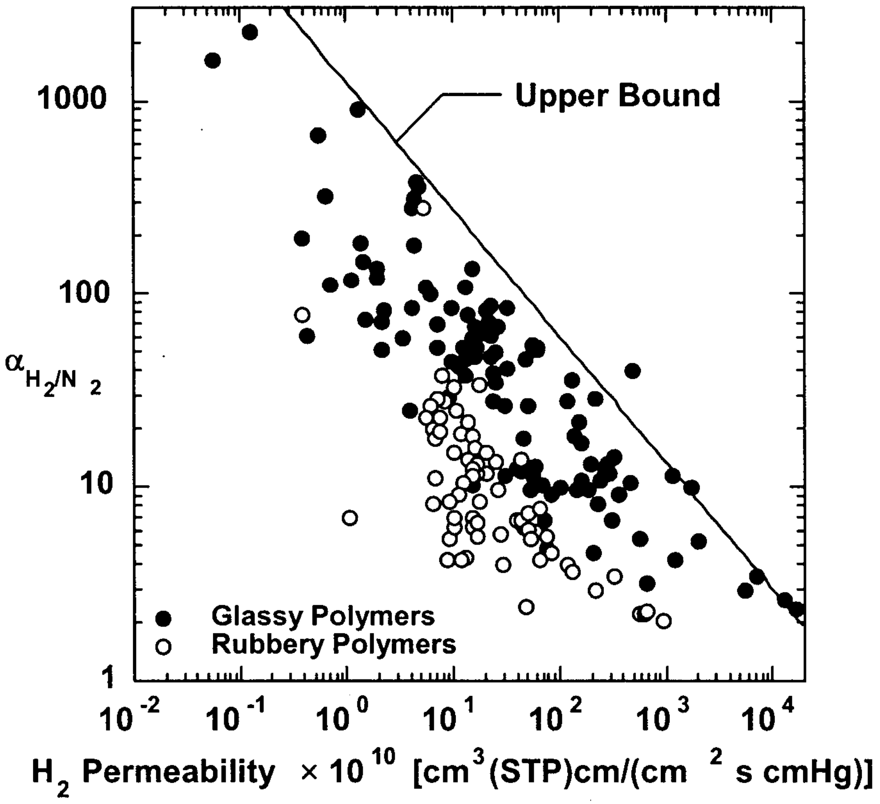
$$\frac{S_{\text{Small}}}{S_{\text{Large}}} > 1 \text{ or } < 1 \qquad \frac{D_{\text{Small}}}{D_{\text{Large}}} >> 1$$

$$\therefore \quad \alpha > 1$$

- Most commercial gas separation polymers (polysulfone, cellulose acetate, polyimide, polyamide) are glassy, have high selectivity due to high diffusivity selectivity and are used for:
  - Production of N_2 enriched air (up to 99.9% pure)
  - Removal of acid gases (CO_2, H_2S) from natural gas
  - Recovery of H_2 from mixtures with hydrocarbons (petrochemical processing) or mixtures with N_2 (ammonia purge gas separation)

Permeability/Selectivity Tradeoff in Size-Selective Polymers:

$$\alpha_{A/B} = \beta_{A/B} / P_A^{\lambda_{A/B}}$$



L. Robeson, Correlation of Separation Factor versus Permeability for Polymeric Membranes, *J. Membrane Sci.*, 62, p. 165 (1991).

Prediction of $\beta_{A/B}$ and $\lambda_{A/B}$

$\alpha_{A/B} = \beta_{A/B} / P_A^{\lambda_{A/B}}$

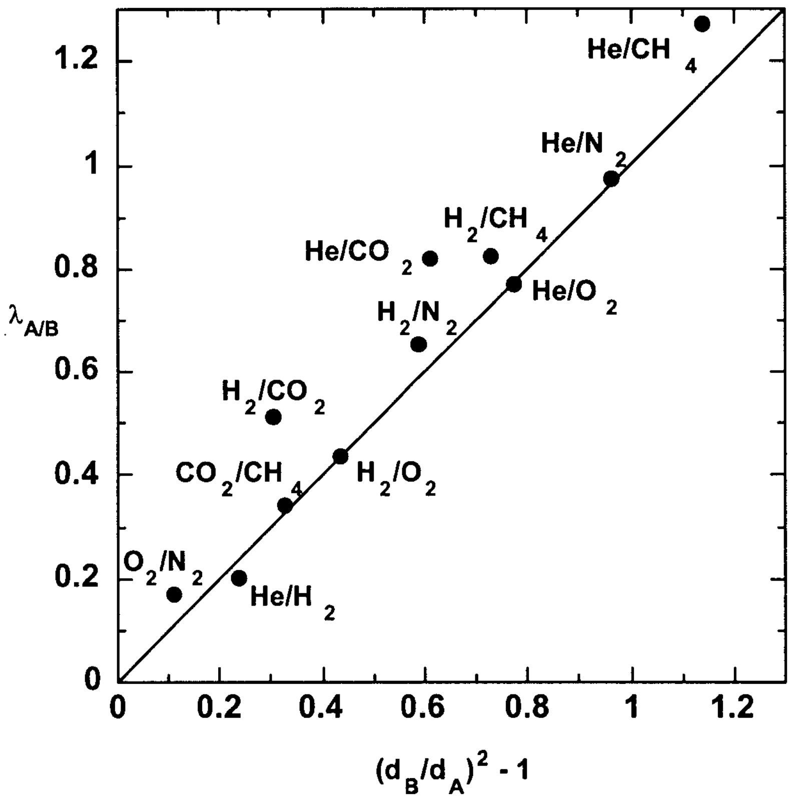
- $P_A = S_A \times D_A$: Solution-Diffusion
- $D_A = D_{o_A} \exp(-E_{D_A}/RT)$: Activated Diffusion
- $\ln D_{o_A} = a(E_{D_A}/RT) - b$: Linear Free Energy
- $E_{D_A} = c d_A^2 - f$: Strongly Size-Sieving
- $S_A = \exp(M + N\varepsilon_A/k)$: Dispersion Forces Control Solubility

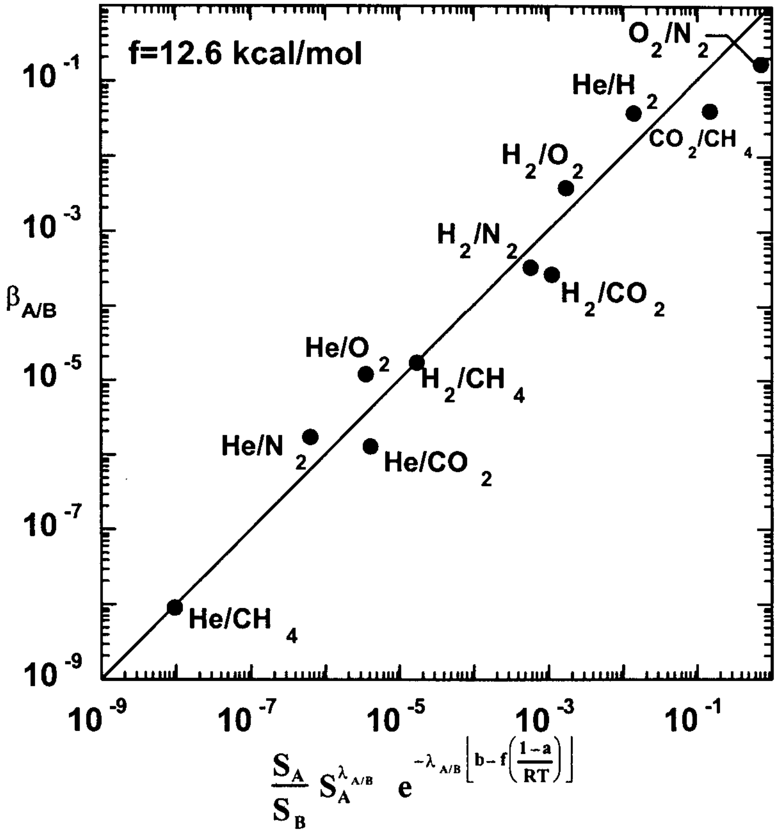
Results:

$$\lambda_{A/B} = \left(\frac{d_B}{d_A}\right)^2 - 1 \qquad \beta_{A/B} = \exp\left(N\left\{(1+\lambda_{A/B})\frac{\varepsilon_A}{k} - \frac{\varepsilon_B}{k}\right\} + \lambda_{A/B}\left(M - b + f\left[\frac{1-a}{RT}\right]\right)\right)$$

B.D. Freeman, Basis of Permeability/Selectivity Tradeoff Relations in Polymeric Gas Separation Membranes, *Macromolecules,* 32(2), pp. 375-380, 1999.

Comparison of Theory with Experiment
$\alpha_{A/B}=\beta_{A/B}/P_A^{\lambda_{A/B}}$

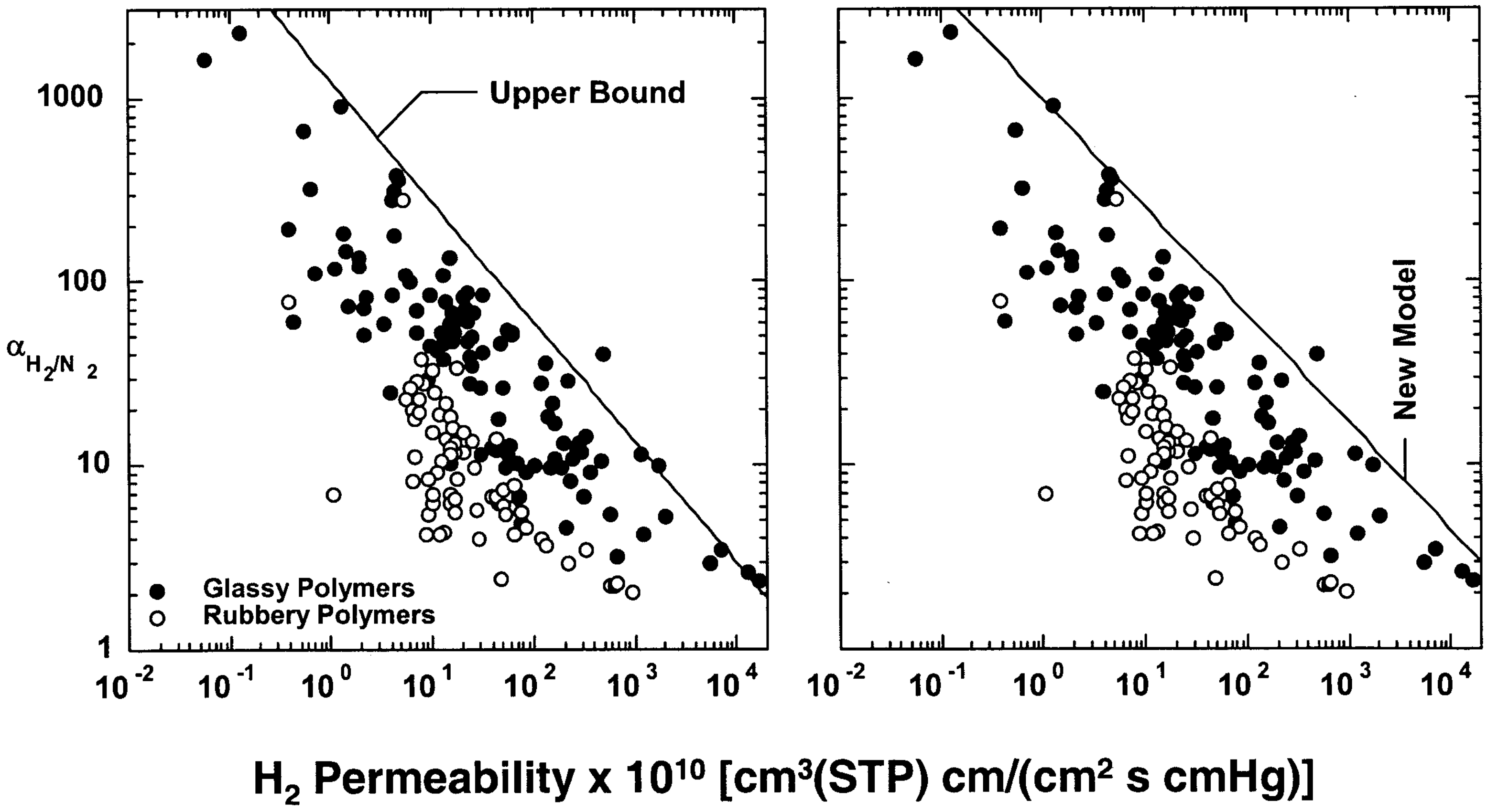




B.D. Freeman, *Macromolecules*, 32(2), 375-380, 1999.

units of $\beta_{A/B}$ are $[\mathrm{cm^3(STP)cm/(cm^2\ s\ cmHg)}]^{\lambda_{A/B}}$

Comparison of Empirical Upper Bound with Theoretical Prediction



Improvement in P/α characteristics by polymer modification

Heuristic: P/α properties improved by structure modifications that increase chain stiffness while increasing interchain separation (*i.e.* free volume).

$$E_{D_A} = cd_A^2 - f$$

c increases with increasing chain stiffness

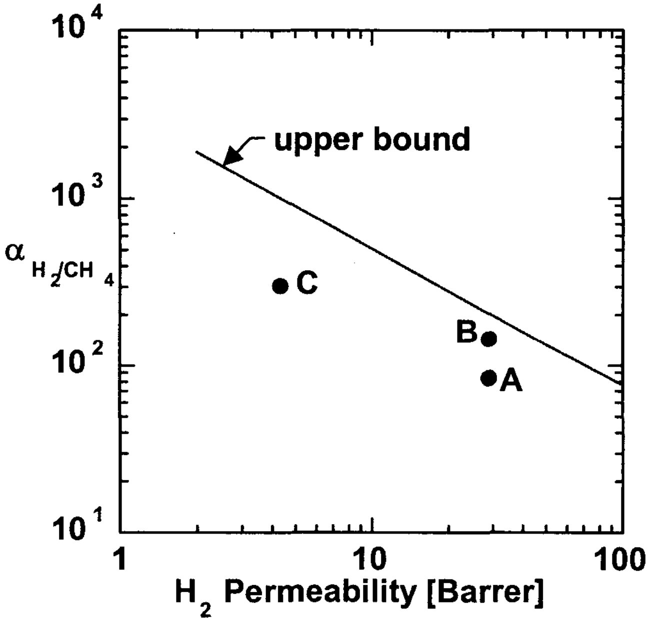
f increases with increasing interchain separation

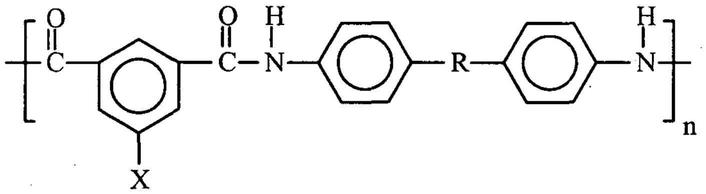
$$P_A = S_A D_A = S_A \exp[-b] \exp\left[\frac{1-a}{RT} f\right] \exp\left[-c \frac{1-a}{RT} d_A^2\right]$$

$$\alpha_{A/B} = \frac{S_A}{S_B} \frac{D_A}{D_B} = \frac{S_A}{S_B} \exp\left[c \frac{1-a}{RT} \left(d_B^2 - d_A^2\right)\right]$$

Influence of chain stiffness and free volume on P/α characteristics

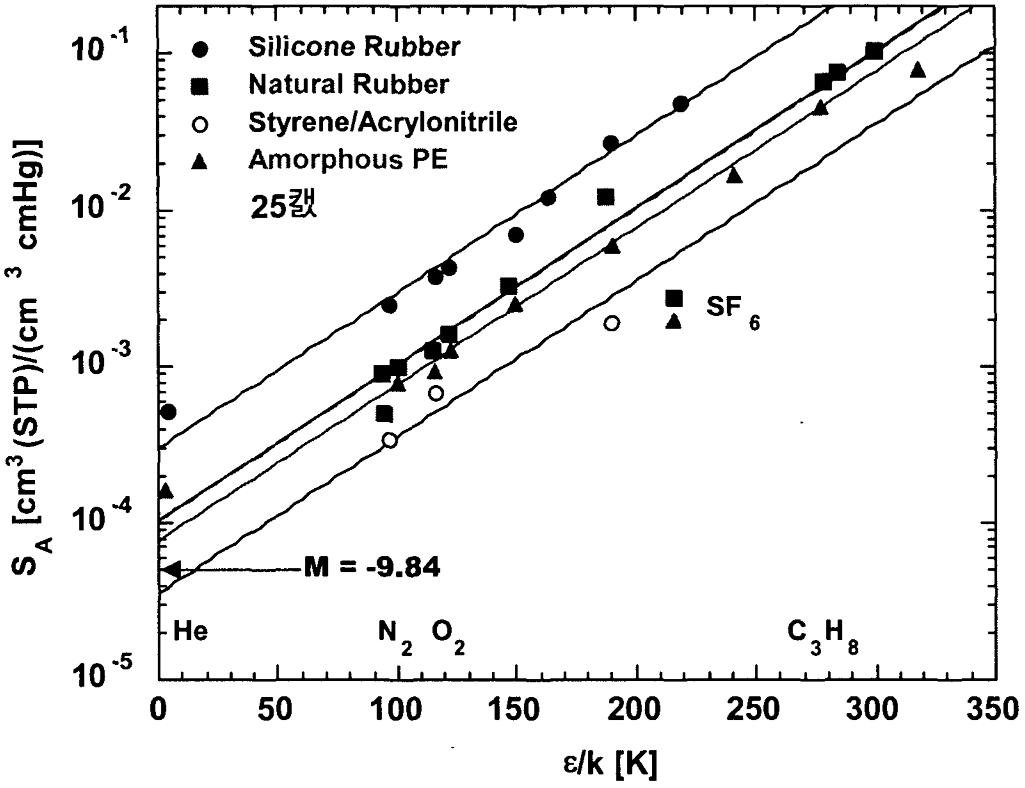
	X	R	T_g [캜]	FFV	P_{H_2}	H_2/CH_4 Selectivity
A	$Si(CH_3)_3$	SO_2	273	0.123	29	85
B	H	$C(CF_3)_2$	297	0.149	29	145
C	H	SO_2	323	0.100	4.3	307





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

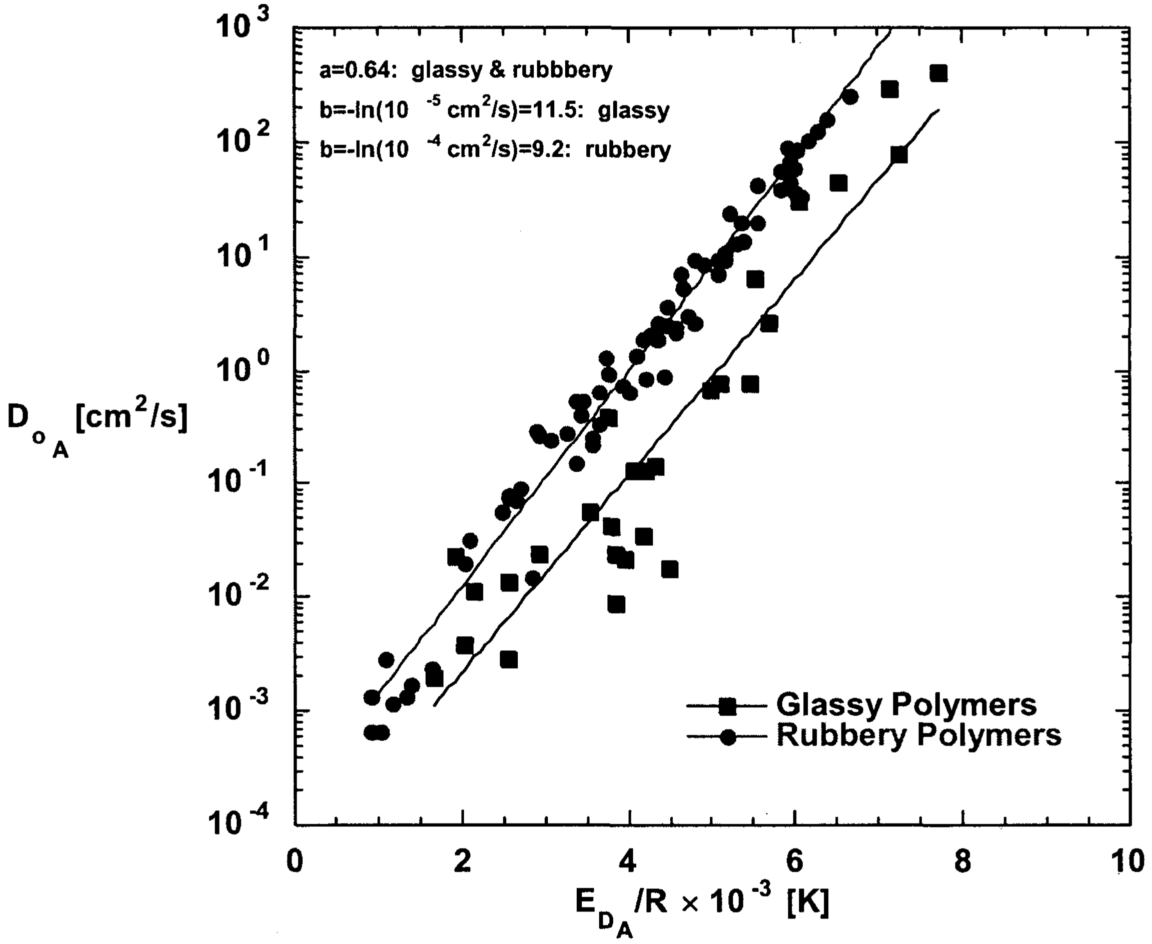
Correlation of Solubility with ε/k: $\ln S_A = M + 0.023\ \varepsilon/k$



D. VanKrevelen, Properties of Polymers: Their Correlation with Chemical Structure; Their Numerical Estimation and Prediction from Additive Group Contributions, Elsevier, Amsterdam, p. 875, 1990.
A. S. Michaels and H. J. Bixler, Solubility of Gases In Polyethylene, *J. Polym. Sci.*, **50**, p. 393 (1961).

Correlation Between E_{D_A} and D_{o_A}:

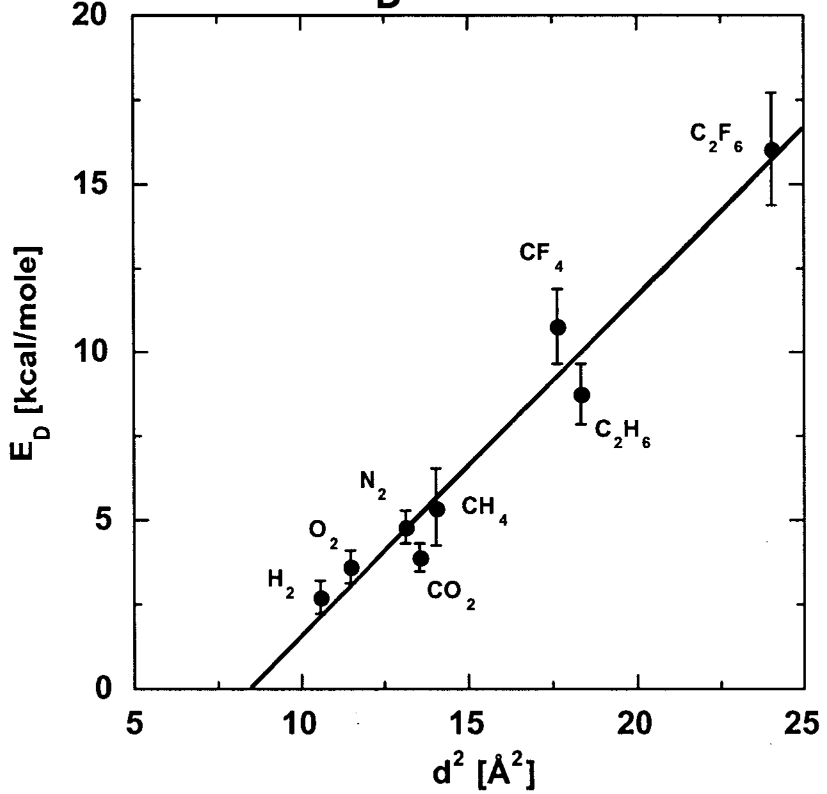
Linear Free Energy Relation: $\ln D_{o_A} = a(E_{D_A}/RT) - b$



D. VanKrevelen, Properties of Polymers: Their Correlation with Chemical Structure; Their Numerical Estimation and Prediction from Additive Group Contributions, Elsevier, Amsterdam, p. 875, 1990.

Effect of Penetrant Size on Activation Energy of Diffusion

$$E_D = cd^2 - f$$



Merkel, T.C., V. Bondar, K. Nagai, and B.D. Freeman, "Gas Sorption, Diffusion and Permeation in Poly(2,2-bistrifluoro-methyl-4,5-difluoro-1,3-dioxole-*co*-tetrafluoroethylene)," *Macromolecules,* **32(25)**, 8427-8440 (1999).

Directions for Improved Polymer Membranes based on High Diffusivity Selectivity

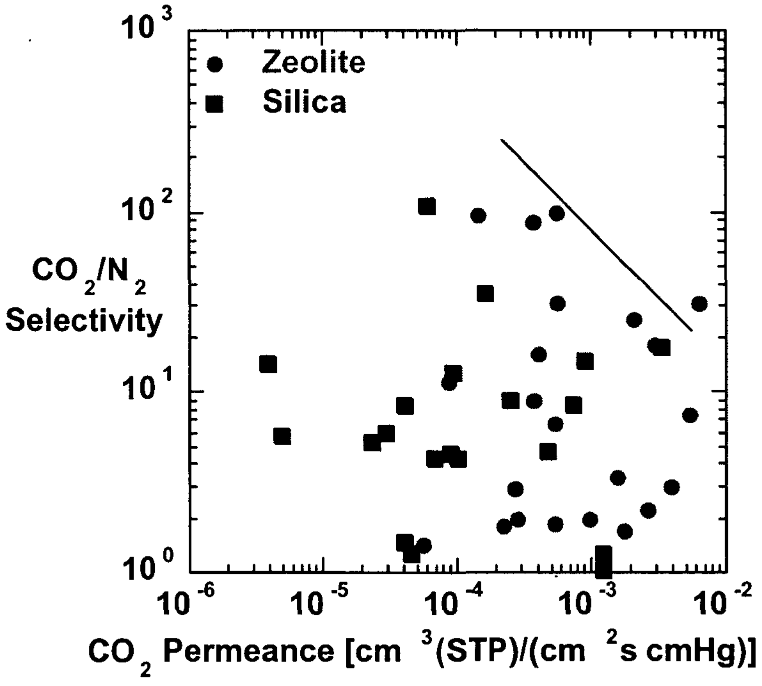
- Tradeoff curves are inevitable as long as the transport mechanism does not change. Improvement in pure gas P/α properties by polymer modification alone will be slow.
- Polymers on or near the upper bound with better chemical and thermal resistance would be useful.
- Polymers as matrices for high performance inorganic materials could be useful processing aid to develop hybrid membranes beyond polymeric upper bound limitations.

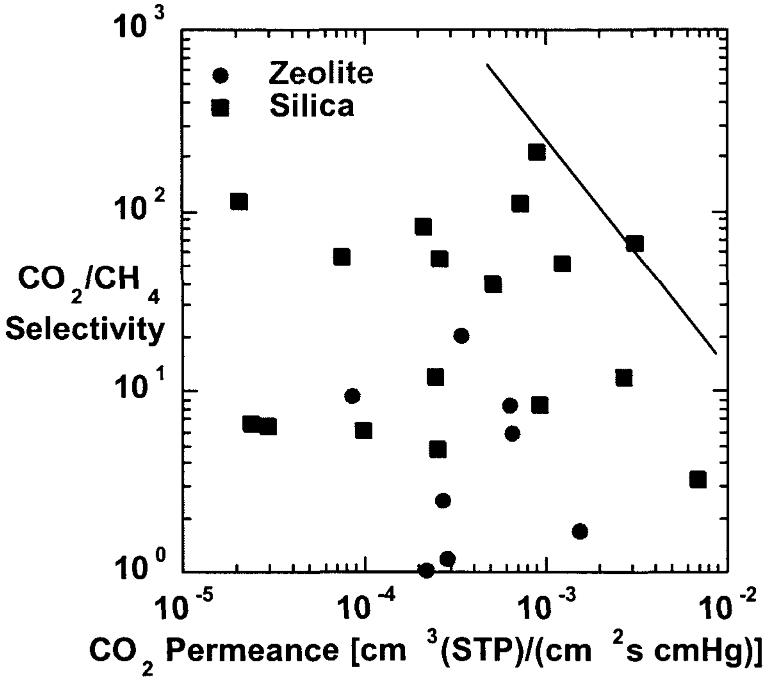
Improved P/α for Strongly Size-Sieving Separations: Inorganic Membranes

Advantages:
High Chemical/Thermal Stability
Stronger Size/Shape Discrimination than Polymers, possibly

Drawbacks:
Expensive
Difficult to Process to High S/V, Defect-Free Modules

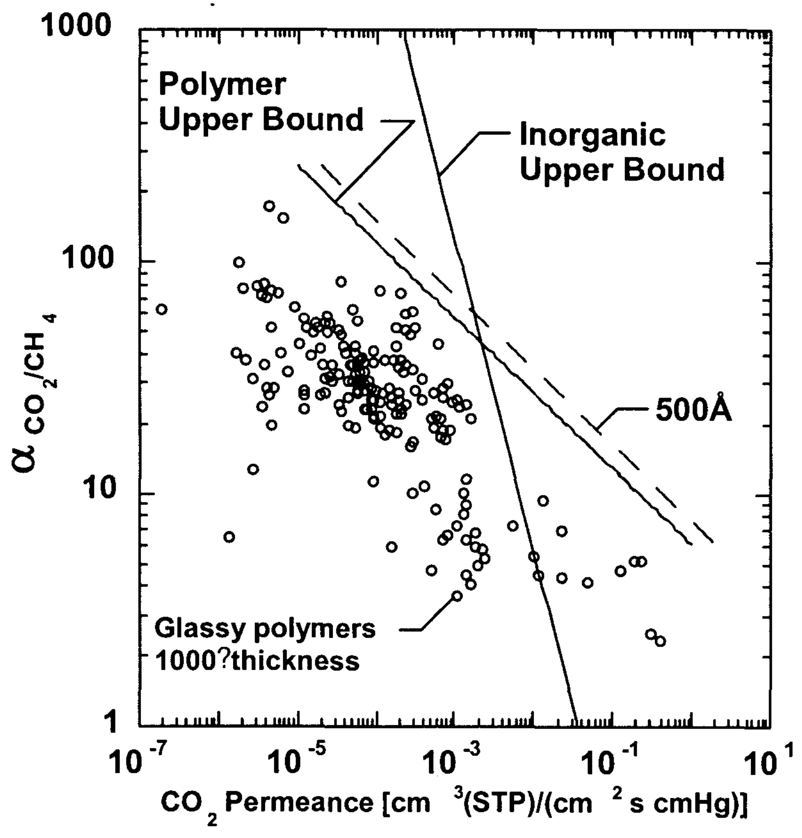
Inorganic Membrane Tradeoff Rules





S. Morooka & K. Kusakabe, "Microporous Inorganic Membranes for Gas Separation," MRS Bulletin, pp. 25-35 (March 1999).

Comparison of Upper Bound Polymers with Inorganics



Synthesis Gas Plant

Cogeneration and H2/CO plants

Rotterdam site, Holland

Synthesis Gas Production

- >90% of world's H_2 produced via hydrocarbon steam reforming:

$$C_nH_m + nH_2O + heat \Leftrightarrow nCO + (\frac{m}{2} + n)H_2$$

$$CO + H_2O \Leftrightarrow CO_2 + H_2$$

- Carbon sources (e.g., coal) contain impurities that appear in syngas product (e.g., H_2S, COS,SO_2).
- Membranes for syngas purification should be more permeable to contaminants (e.g., H_2S, CO_2) than to H_2 to produce high pressure, high purity syngas product.

Physical Properties of Key Syngas Components

Penetrant	Size	Condensability
	Critical Volume, cm^3/mole	Critical Temperature, K
H_2	65.1	33.2
CO	93.1	132.9
CO_2	93.9	304.2
H_2S	98.6	373.2

CO_2 and H_2S have much higher critical temperatures than H_2 or CO. This difference in critical temperatures makes them ideal candidates for separation using “solubility selective” polymer membranes.

Separation Based on High Solubility Selectivity

$$P = S \times D$$

$$\alpha = \frac{P_{acid\ gas}}{P_{H_2}} = \frac{D_{acid\ gas}}{D_{H_2}} \frac{S_{acid\ gas}}{S_{H_2}}$$

$$\frac{S_{acid\ gas}}{S_{H_2}} >> 1 \qquad \frac{D_{acid\ gas}}{D_{H_2}} < 1$$

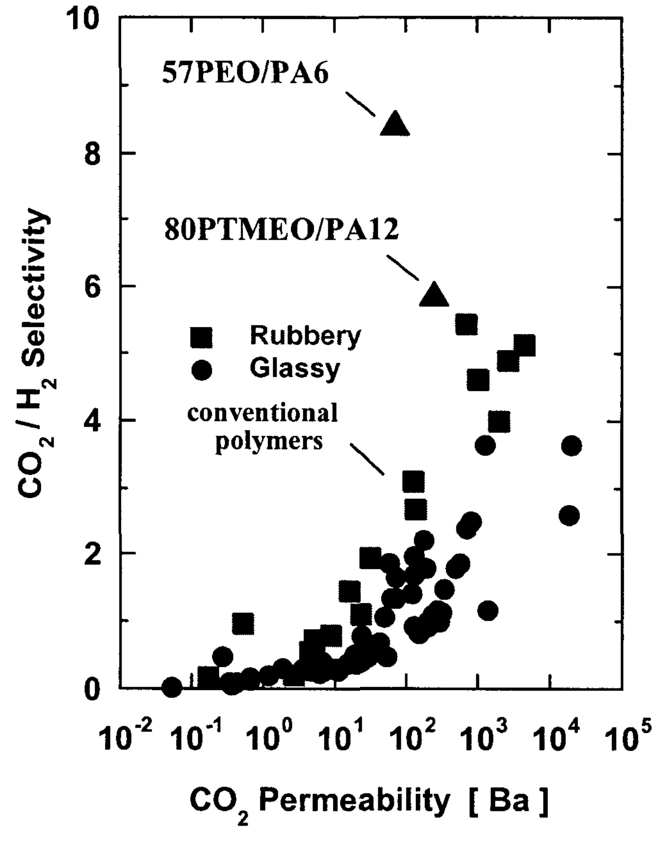
$$\therefore \quad \alpha > 1$$

Optimum Materials Characteristics:

Weak size-sieving ability

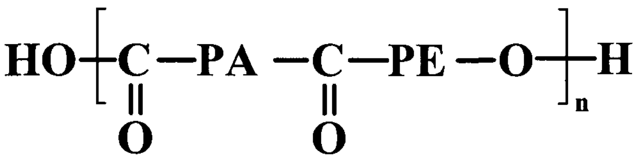
Specific, favorable interactions between acid gas and polymer matrix

Improve P/α in Solubility-Selective Polymers: Modify polymer matrix to enhance solubility of more soluble components



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

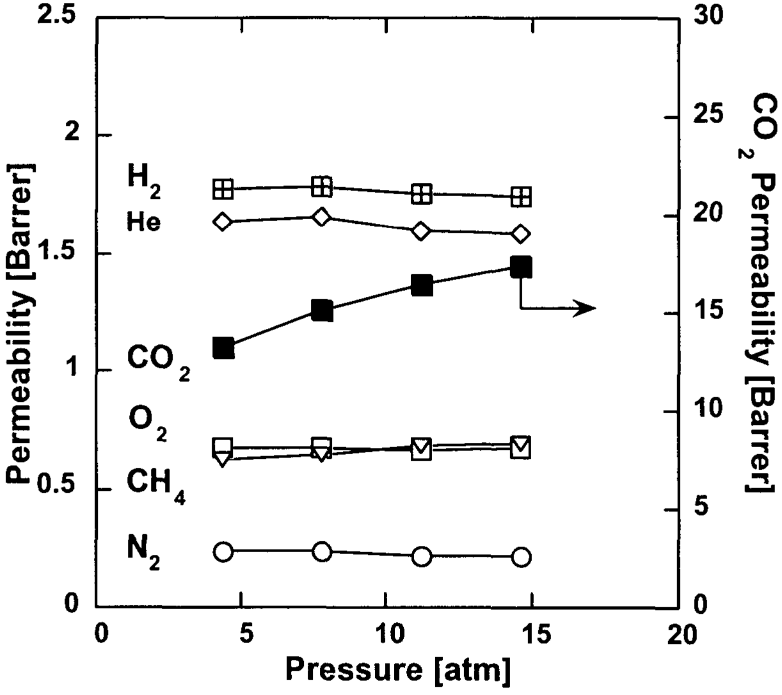
Pebax:

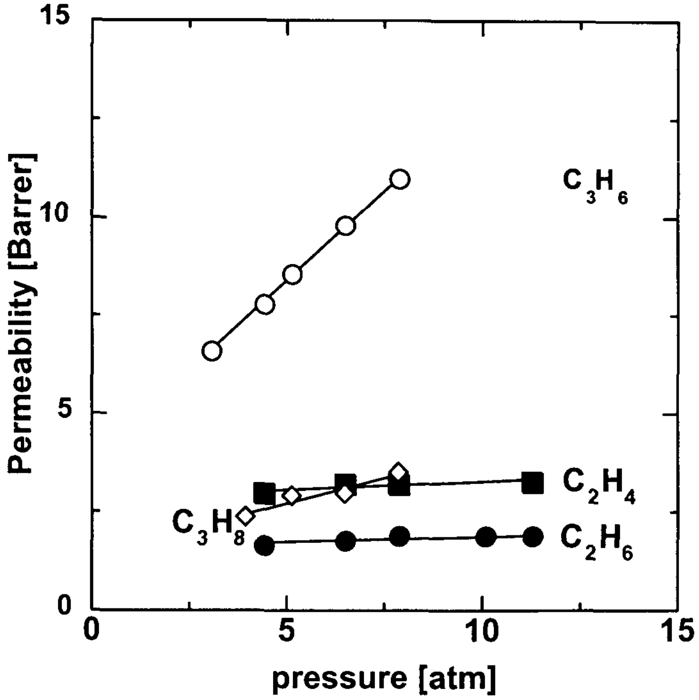


$$\mathrm{HO}\left[\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{PA}-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{PE}-\mathrm{O}\right]_n\mathrm{H}$$

Segmented block copolymers containing highly permeable, rubbery, polar polyether (PEO or PTMEO) phase dispersed in glassy, low permeability polyamide (PA6 or PA12) phase.

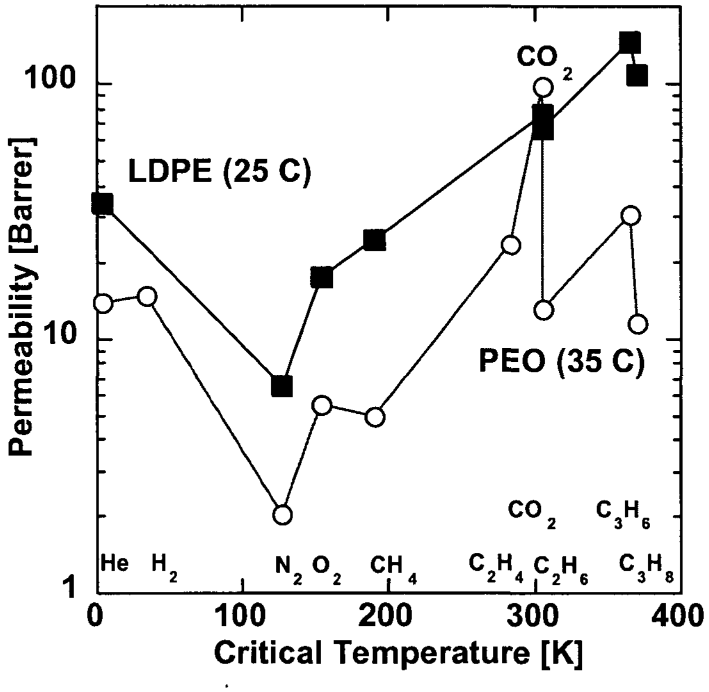
Permeation Properties of PEO $(CH_2\text{-}CH_2\text{-}O)_n$





35 °C, 65 wt. % crystallinity

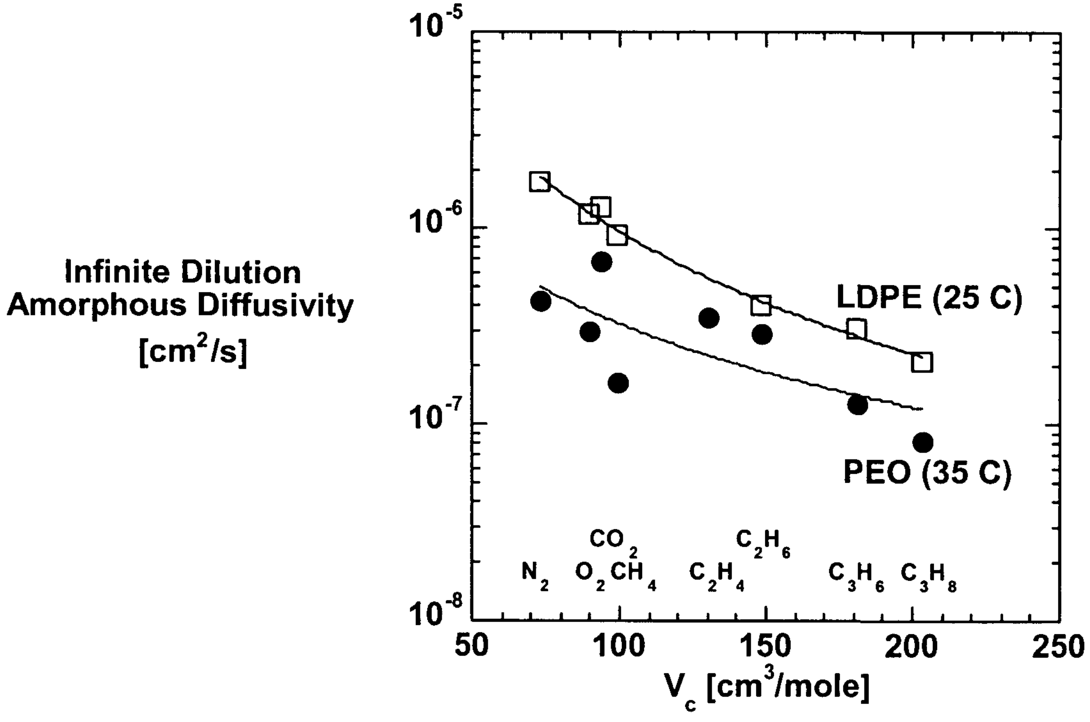
Effect of Ether Linkage on Permeability



	CO_2/He
LDPE	2.5
PEO	7

Permeability coefficients corrected to amorphous basis using: $P_{semicrystalline}=P_{amorphous}$ x (amorphous volume fraction)^2
Permeability coefficients extrapolated to zero upstream pressure.
LDPE data from: Michaels & Bixler, *J. Polym. Sci.*, **50**, 413, 1961.

Diffusion Coefficients

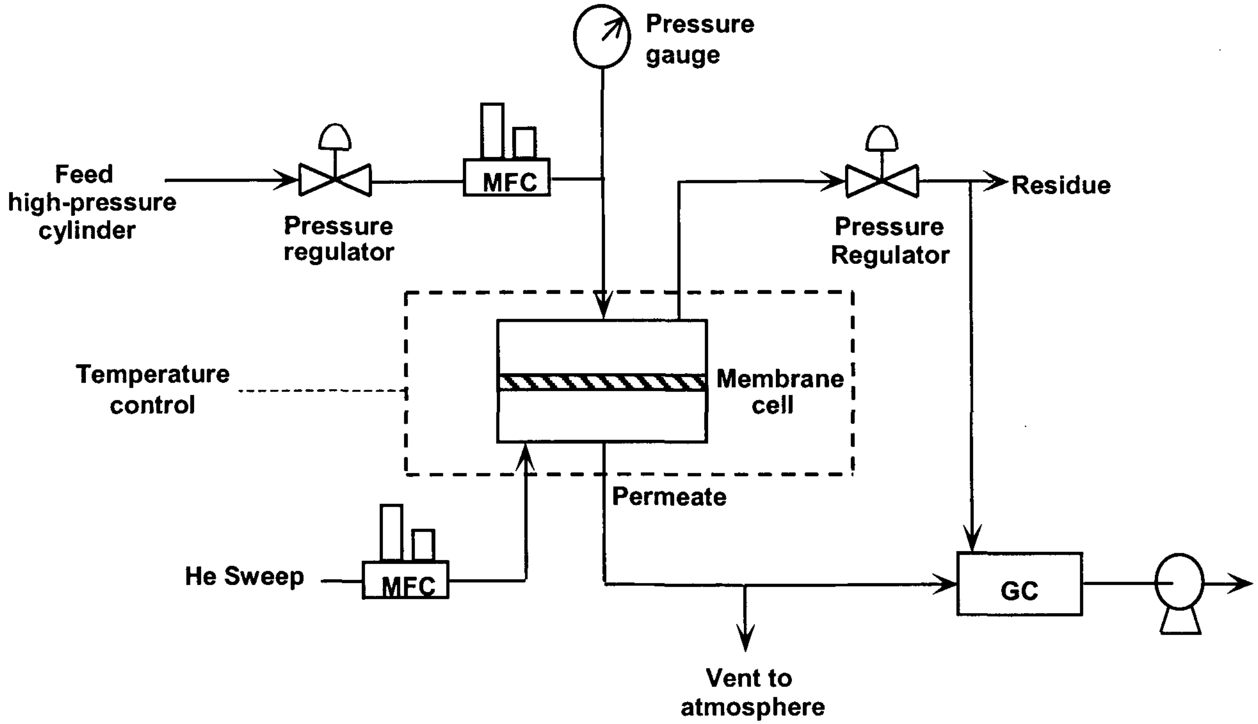


Solubility

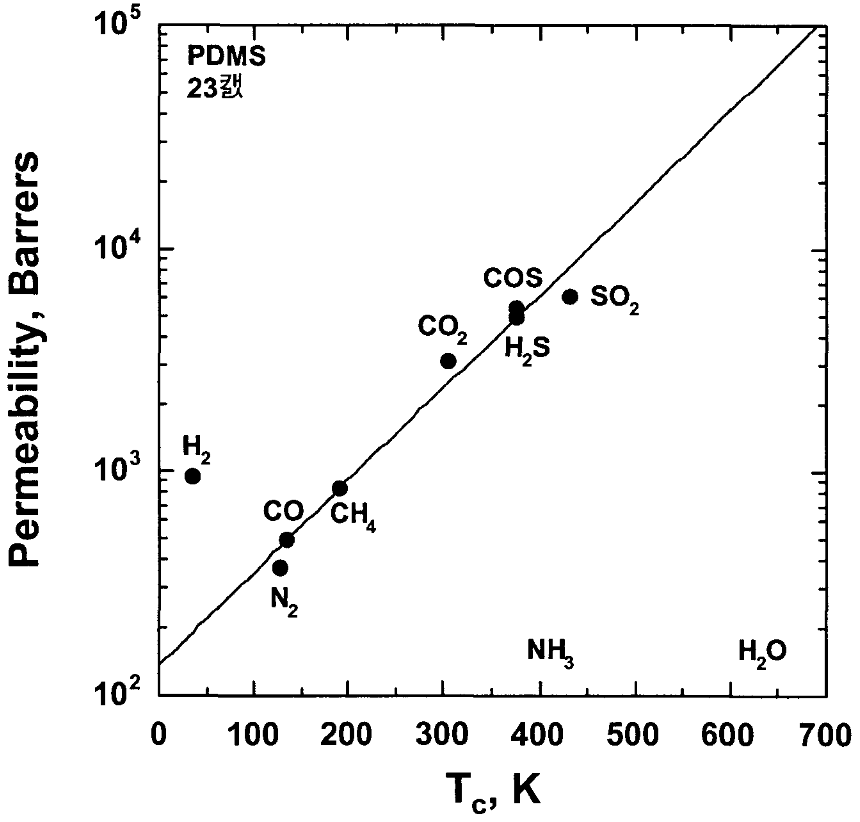
	CO_2/C_2H_6
LDPE	0.35
PEO	3.2

Gas Permeation Apparatus

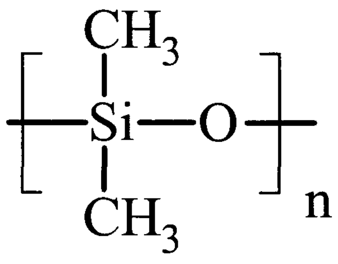
Feed: Simulated Texaco Syngas
42% H_2, 46% CO, 10.5% CO_2, 1.5% H_2S



Permeation of Syngas components in Solubility-Selective Polymer

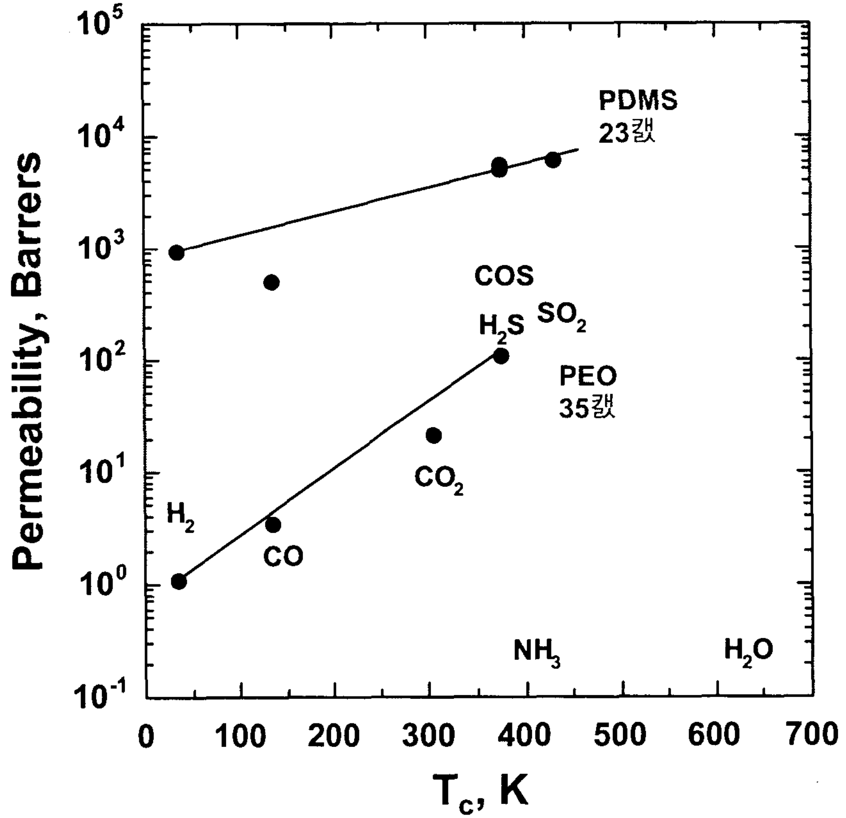


1 Barrer = 10^{-10} cm^3(STP)cm/(cm^2 s cmHg)



$$\left[-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{Si}}}} - O - \right]_n$$

Permeation of Syngas components in Polar Solubility-Selective Polymer

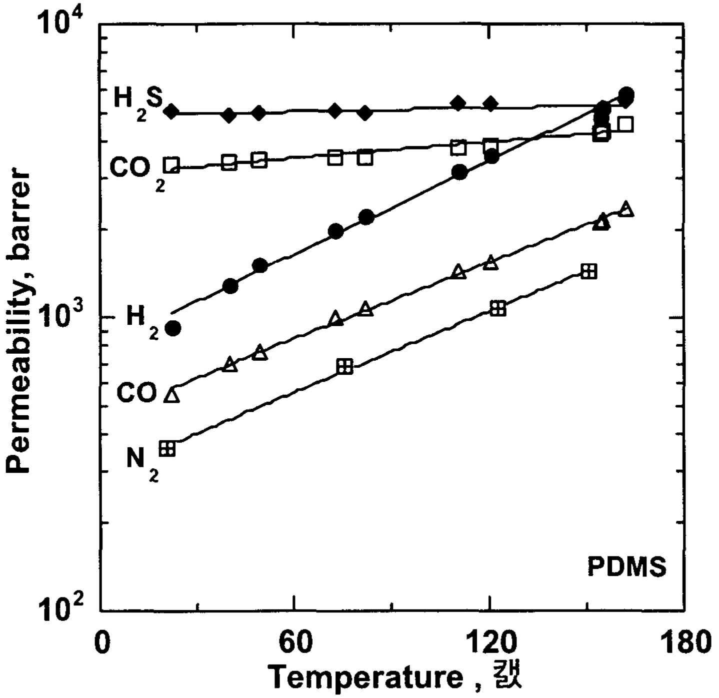


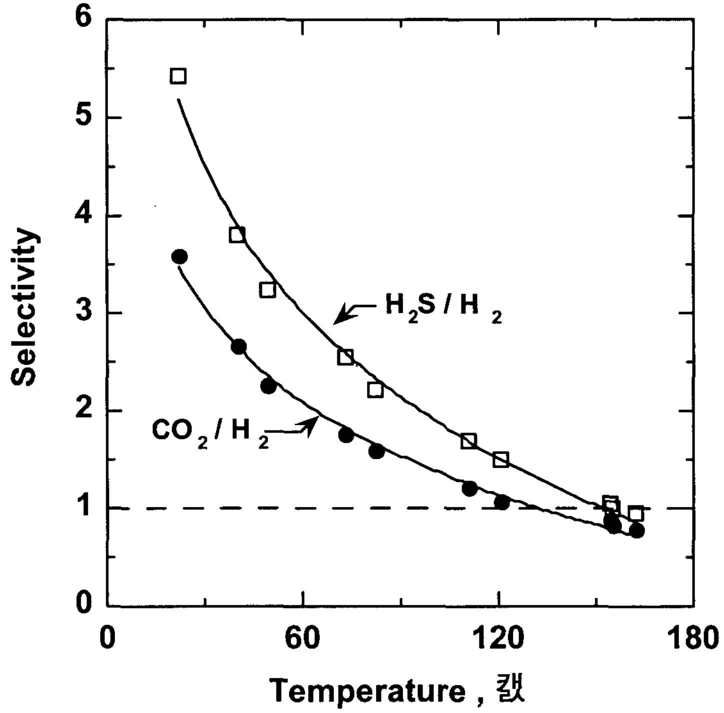
1 Barrer = 10^{-10} cm^3(STP)cm/(cm^2 s cmHg)

$$\left[-CH_2-CH_2-O- \right]_n$$

Polymer	H_2S/H_2 Selectivity
PDMS	5.4
PEO	31

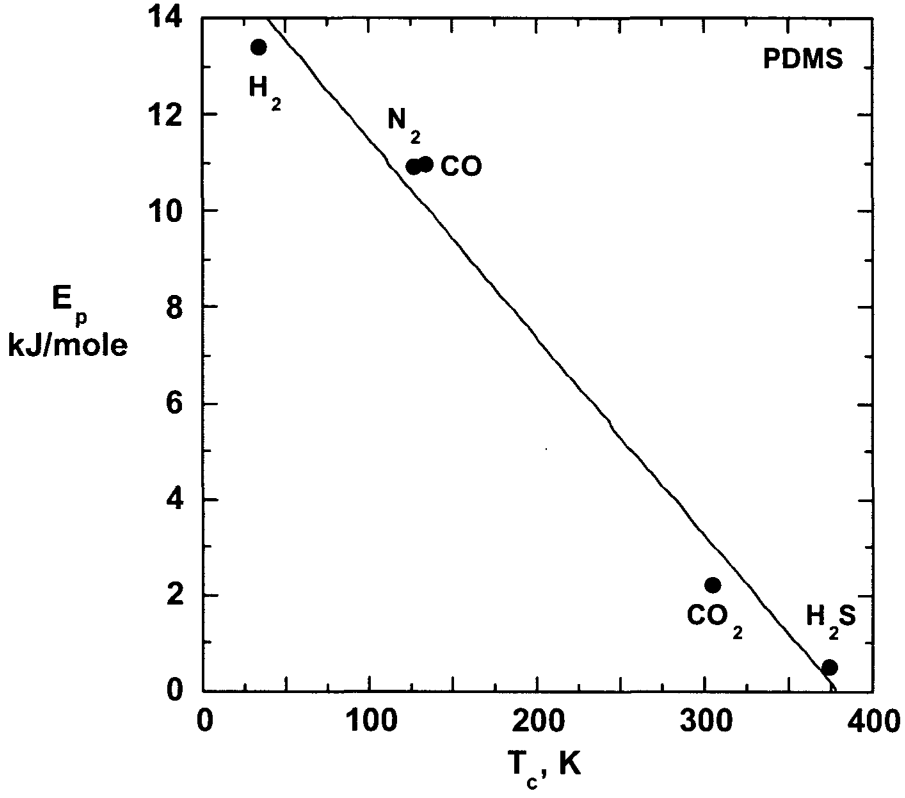
Effect of Temperature on Mixture Permeability & Selectivity in PDMS





Merkel, T.C., *et al., J. Membrane Sci.*, **191(1-2)**, 85-94 (2001).

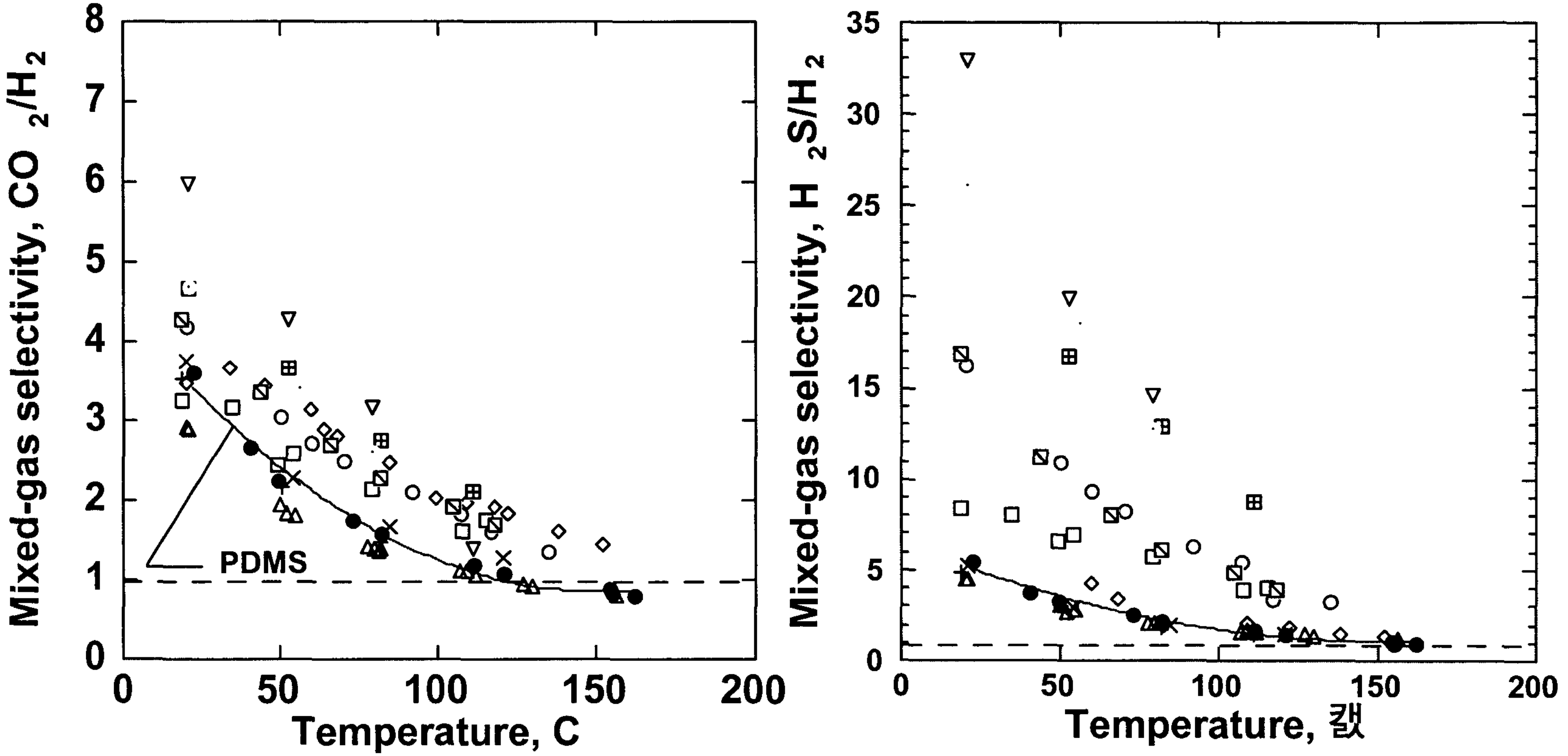
Activation Energy of Permeation in PDMS



$$E_P = \underset{(\text{always} > 0)}{E_D} + \underset{(< 0 \text{ for acid gases, } \sim 0 \text{ for light gases})}{\Delta H_S}$$

Merkel, T.C., *et al., J. Membrane Sci.*, **191(1-2)**, 85-94 (2001).

Effect of Temperature on Mixture Selectivity

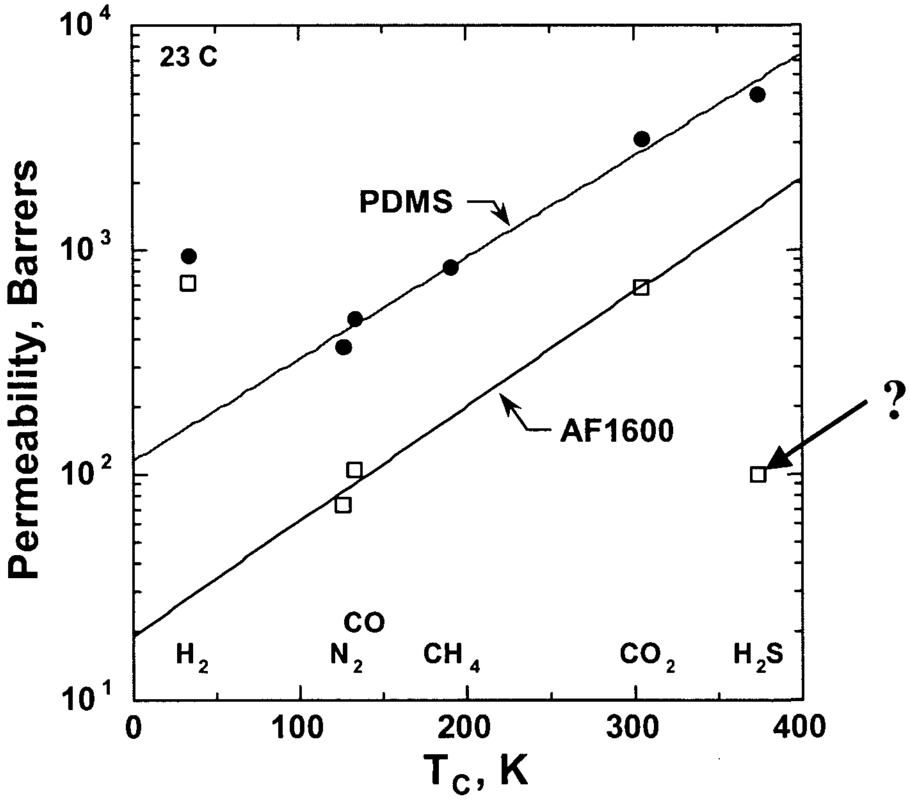


$E_P = E_D + \Delta H_S$

E_D (always > 0)

ΔH_S (< 0 for acid gases, ~0 for light gases)

Unexpectedly Low H_2S Permeability in Fluoropolymers



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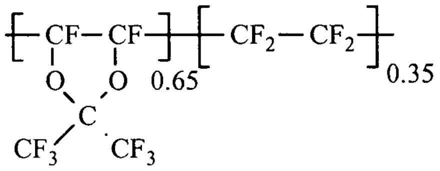
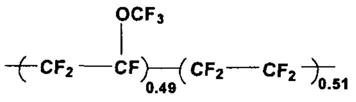


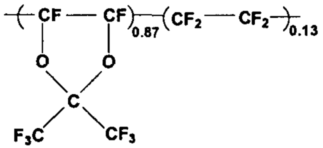
CO_2/H_2S Selectivity in Fluorinated and Non-fluorinated Polymers

Polymer	CO_2 Permeability, barrers	Selectivity CO_2/H_2S
PDMS[a]	3200	0.63
Pebax 1657	69	0.27
Pebax 1074	122	0.22
Cellulose acetate[c]	2.4	1.2
Dupont 9918[b]	28	8.0
AF1600[a]	680	6.8
AF2400[a]	2300	6.0

57 wt. % PEO/ 43 % PA6

55 wt. % PEO/ 45 % PA12





[a] mixed gas feed (42% H_2 / 10.5% CO_2/ 46% CO / 1.5% H_2S), 1% stage cut, 23°C, $\Delta p = 50$ psig.
[b] same as [a] except experimental temperature = 37°C.
[c] data of Stern et al., temperature = 35°C and $\Delta p = 147$ psig.

Conclusions

- Polymers on upper bound curves for diffusivity-selective separations:
    - Sieve penetrants strongly based on size
    - Are stiff-chain materials with large interchain spacings
    - Improvements in chemical, thermal resistance is highly desirable
- Inorganic membranes are also subject to tradeoff rules.
- Permeability of rarely studied gases (*e.g.,* H_2S, CO, COS, SO_2) are consistent with gas molecular properties in hydrocarbon polymers considered.
- H_2S permeability low in fluoropolymers.
- CO_2/H_2 and H_2S/H_2 selectivities decrease with increasing temperature in all materials studied.