



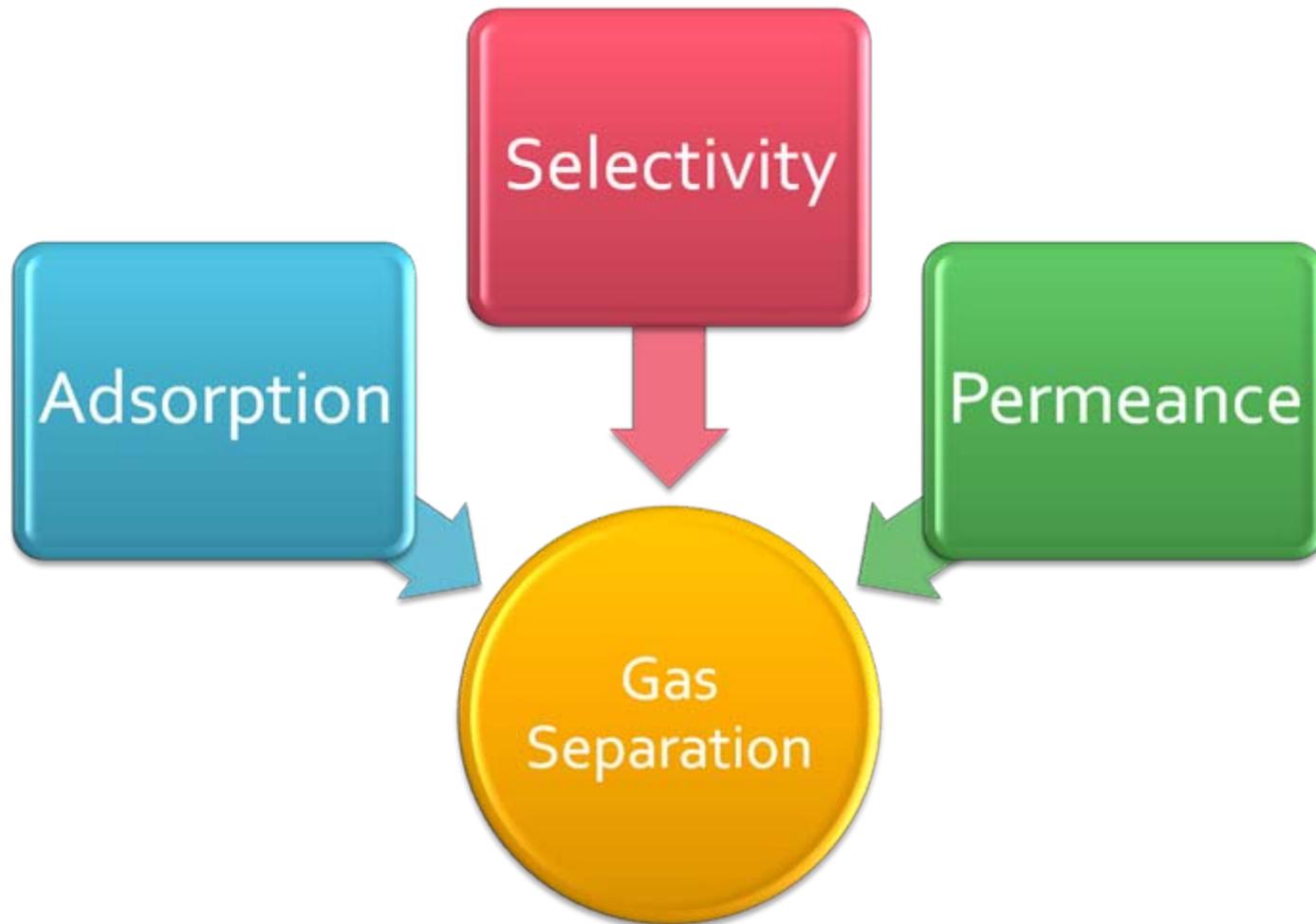
SOUTHERN MISS
GOLDEN EAGLES



Selective Gas Sorption in Metal Organic Frameworks

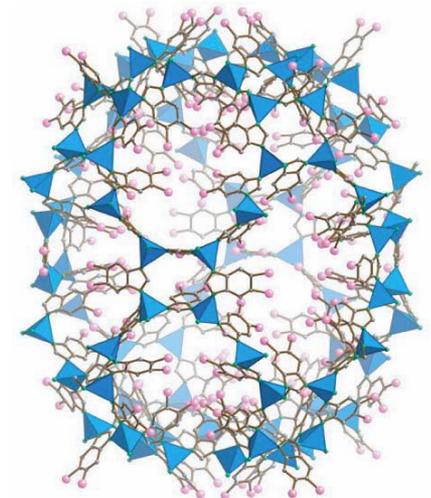
Grant White

Overview



Carbon Capture

- Gas separation is industrially and environmentally important
- Flue gas CO₂ composition ~ 10-20%
- CO₂ Capture: large fraction of CCS program
- Amine Absorbers (\$150/ton)
- Current Focus:
 - Adsorption (physical and chemical)
 - Gas separation membranes

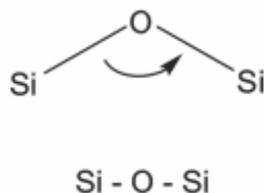
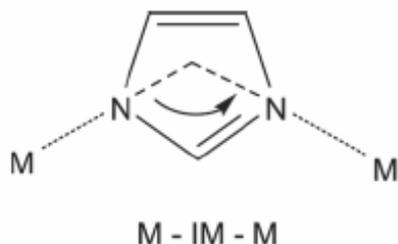


Metal Organic Frameworks (MOFs)

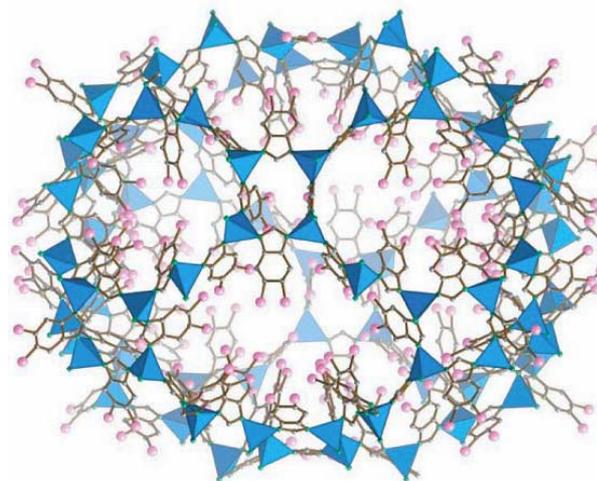
- Metal Organic Frameworks (MOFs)



- Zeolitic Imidazolate Frameworks (ZIFs)



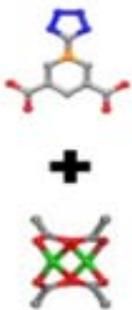
- Benefits of MOFs
 - Large Surface Area
 - Tunable pore sizes, volumes, surface chemistries...



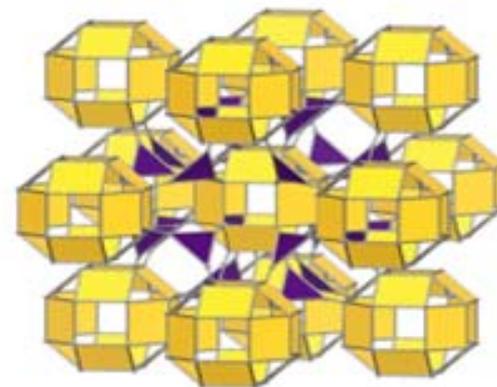
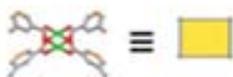
Synthesis of MOFs

- Solvothermal Synthesis: “a chemical reaction in a closed system in the presence of a solvent (aqueous or non-aqueous solution) at a temperature higher than that of the boiling point¹ of such a solvent.” G. Demazeau, J. Mater. Sci., 2008, 43, 2104–2114.

MBBs:



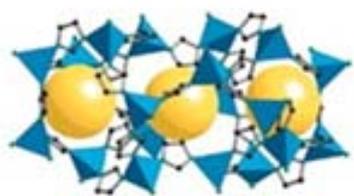
SBBs:



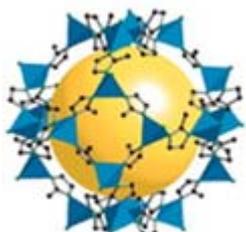
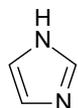
- Typical Solvents: DMF, DEF, DMA, MeOH, H₂O
- Temperature Range: 60 – 160 °C

¹We do not actually go past the BP of DMF (160 °C)

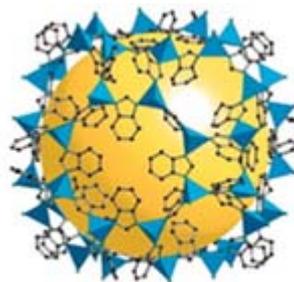
Target Frameworks



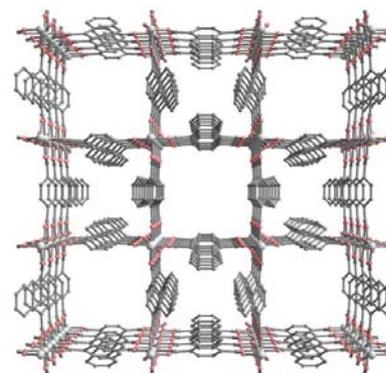
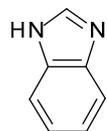
ZIF-4



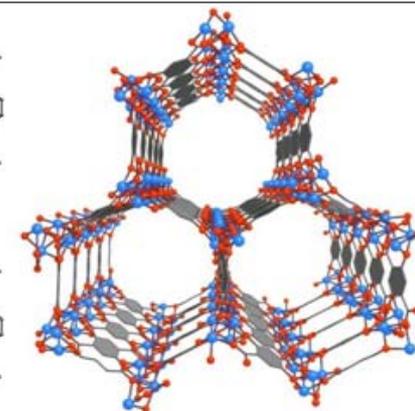
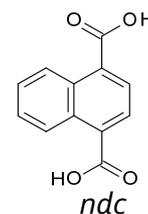
ZIF-8



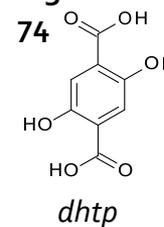
ZIF-11



Al(NDC)



Mg-MOF-74



Framework

Reactants

Pore Size (Å)

ZIF-4

Zinc + Imidazole

2.1

ZIF-8

Zinc + Methylimidazole

11.6

ZIF-11

Zinc + Benzimidazole

14.6

Al(NDC)

Aluminum + ndc

8.5

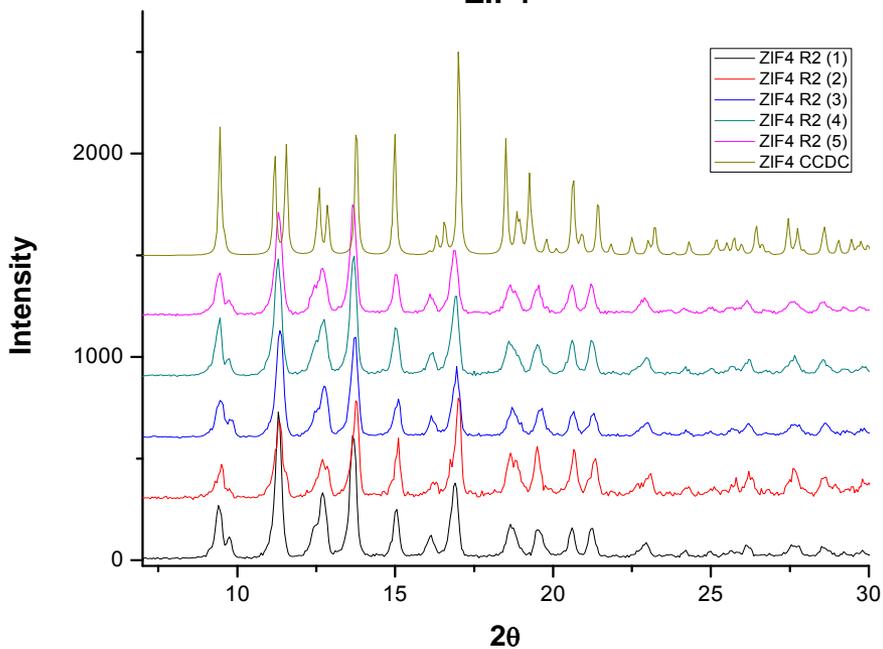
MOF-74

Magnesium + dhtp

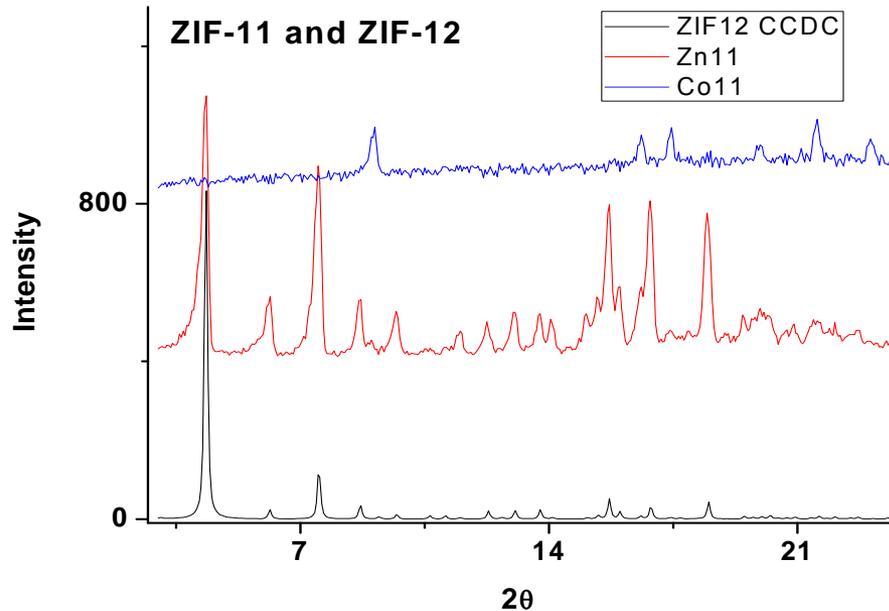
11

X-Ray Diffraction

ZIF4

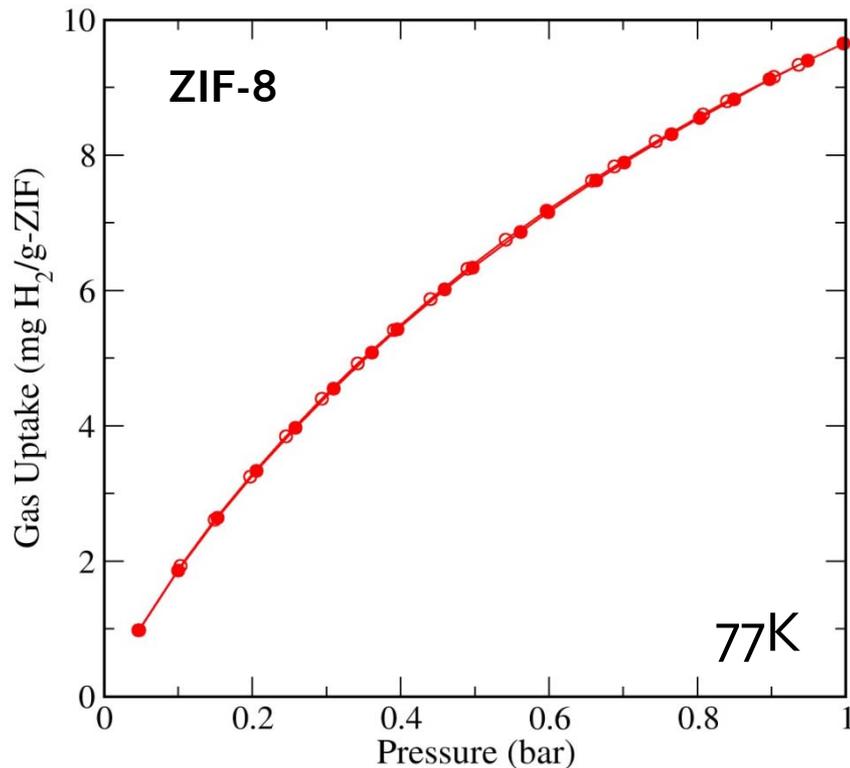


ZIF-11 and ZIF-12



Characterization: Adsorption

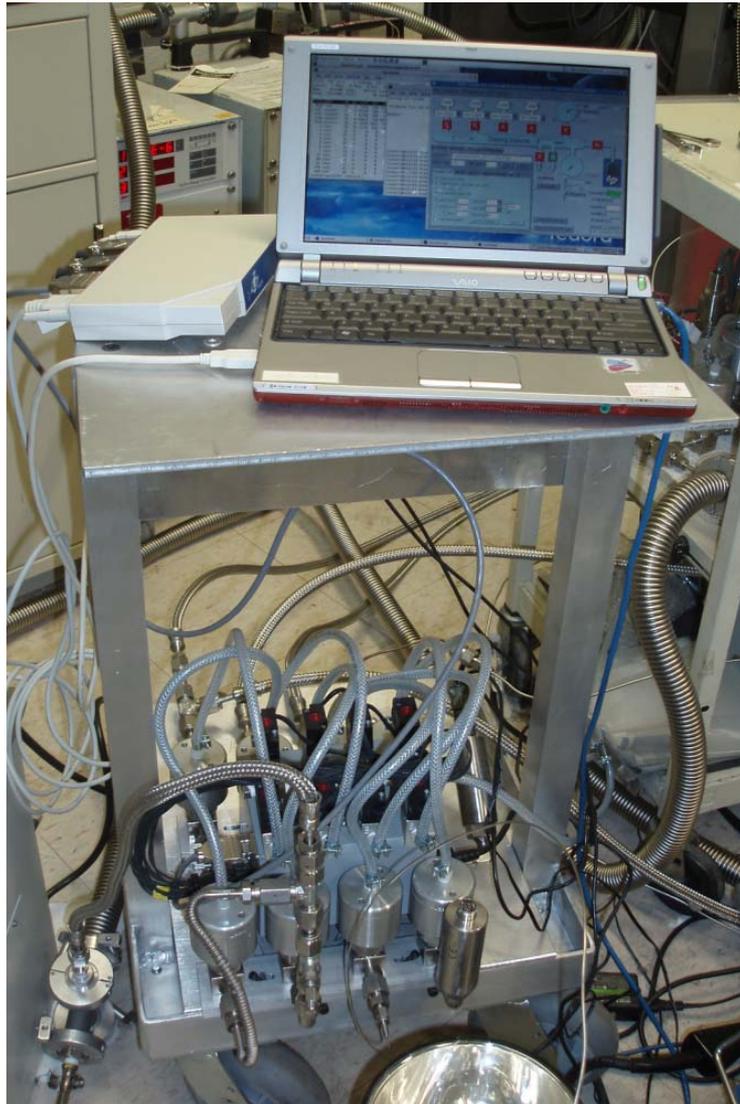
CONFIRM POROSITY WITH PUBLISHED RESULTS



Get Isothermic Heat of Adsorption from multiple t

$$Q_{st} = RT^2 \left(\frac{\partial \ln P}{\partial T} \right)_q$$

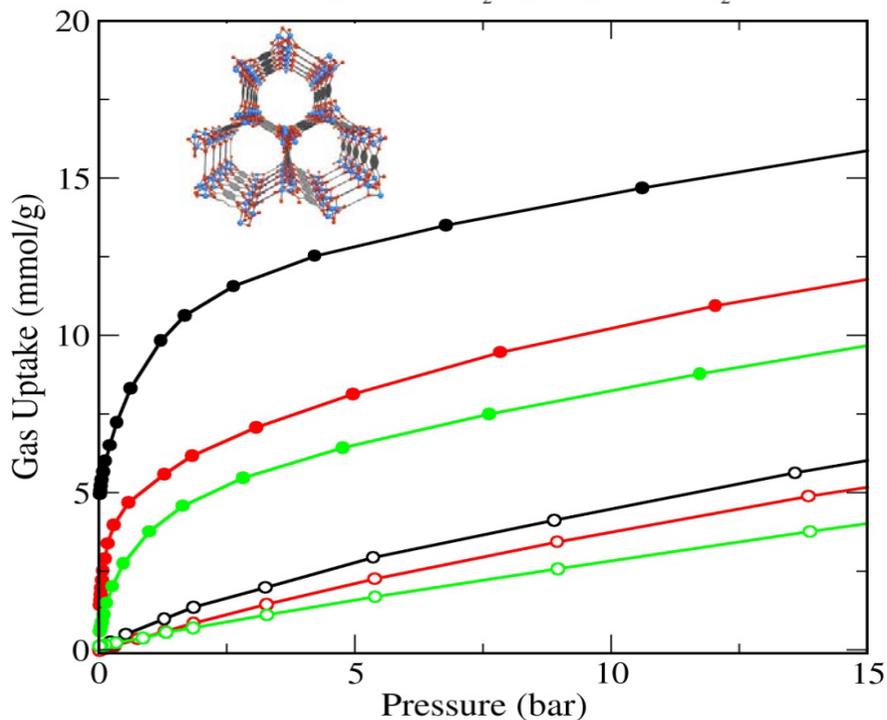
Gas Rig: Adsorption and Permeance



Adsorption Data: MOF-74 vs. ZIF-8

Gas Uptake - MOF74

Closed symbols = CO₂, Open Symbols = N₂



MOF-74

CO₂

N₂

17 mmol/gram

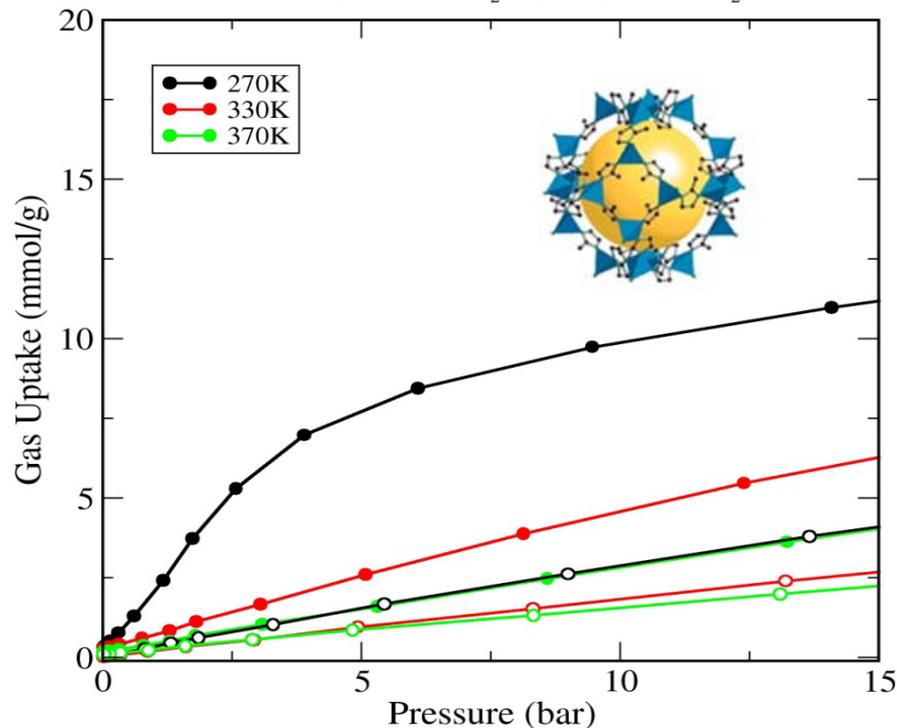
7 mmol/gram

$Q_{st} = 31$ kJ/mol

$Q_{st} = 11.5$ kJ/mol

Gas Uptake - ZIF8

Closed symbols = CO₂, Open Symbols = N₂



ZIF-8

CO₂

N₂

12.5 mmol/gram

5 mmol/gram

$Q_{st} = 19$ kJ/mol

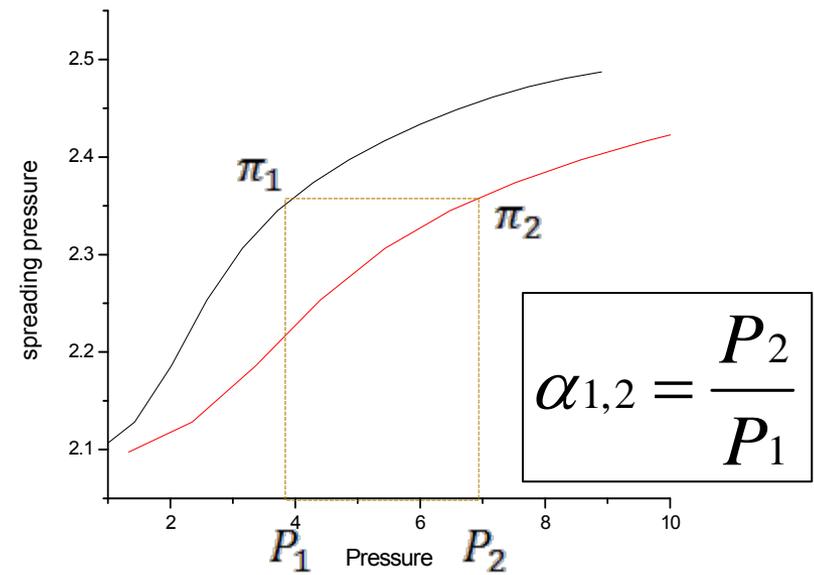
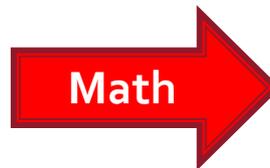
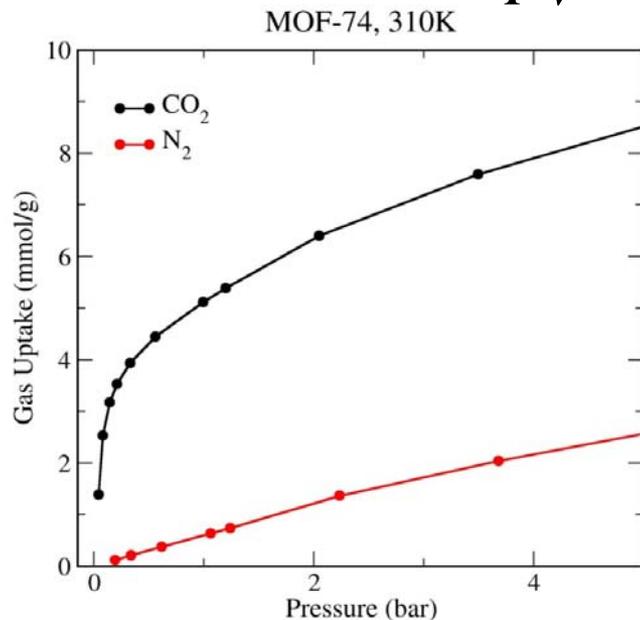
$Q_{st} = 6.5$ kJ/mol

Selectivity Calculations

■ Ideal Adsorbed Solution Theory (IAST)

- Accounts for competition
- Independent of isotherm model
- Agrees with detailed simulations of gas mixtures
- Requires only single component isotherms

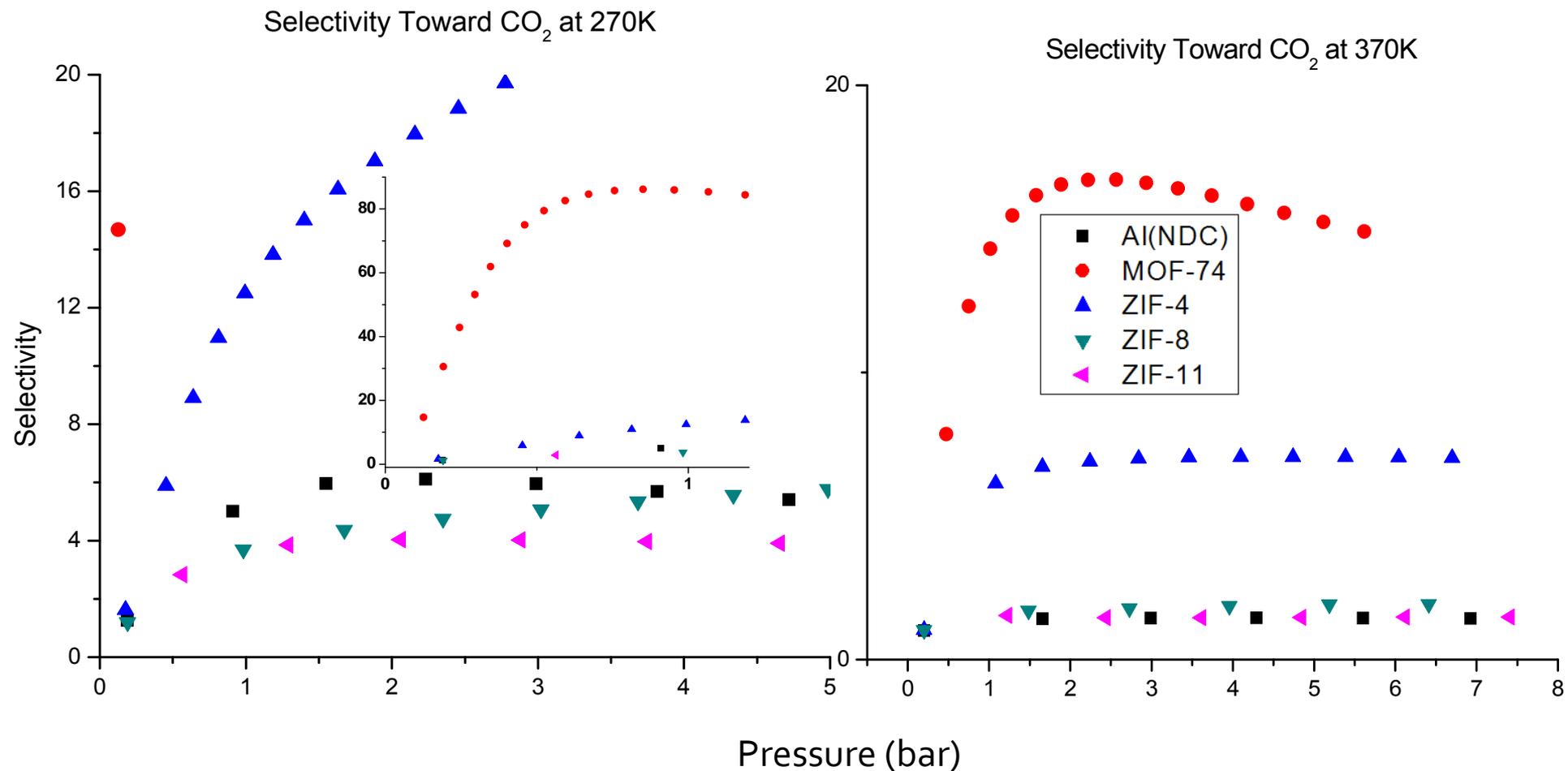
$$PV = nRT \rightarrow \pi A = nRT$$



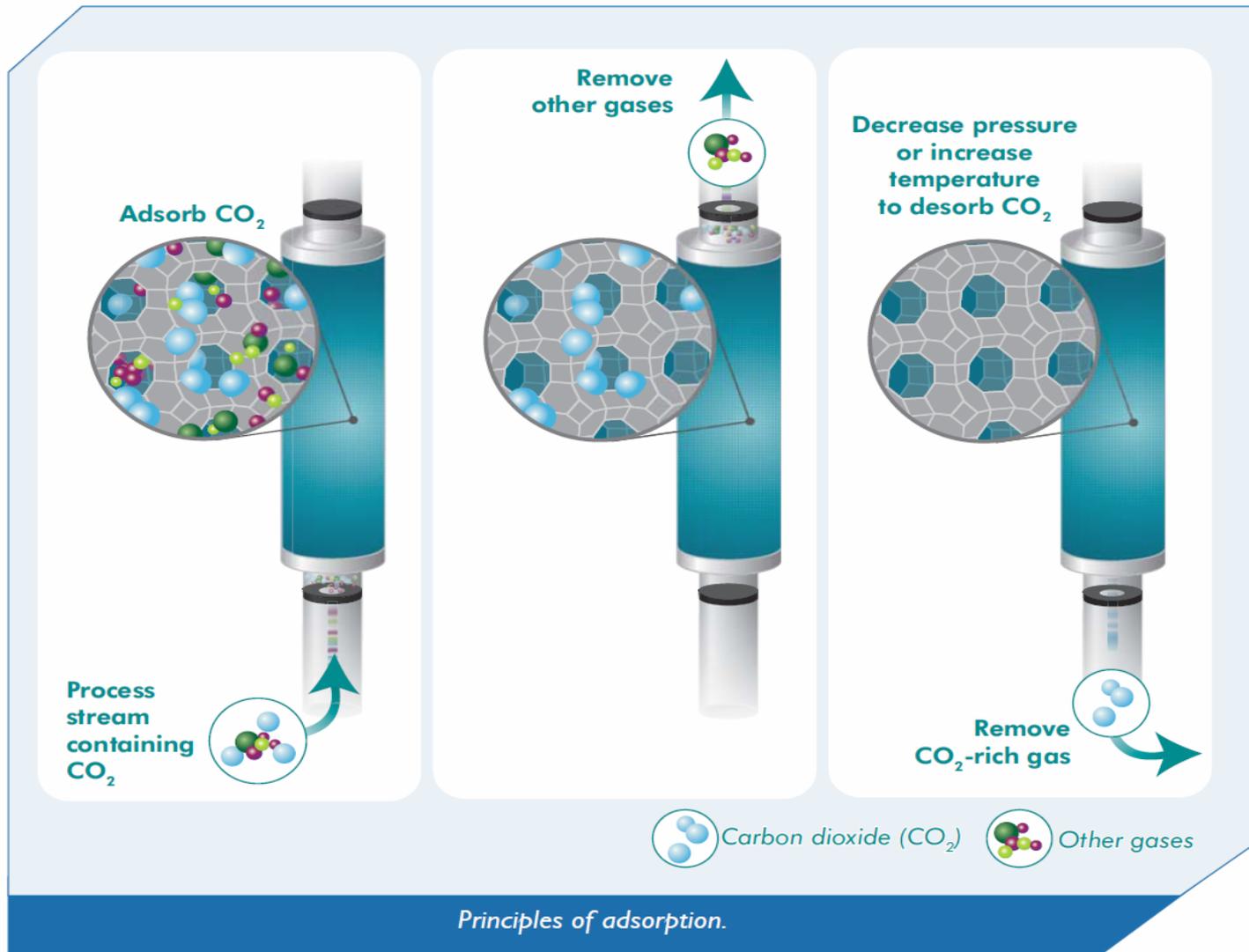
$$\alpha_{1,2} = \frac{P_2}{P_1}$$

- 7 coupled equations, 9 unknowns
- Define gas phase concentration and pressure of mixed gas

Selectivity Data: 20% CO₂

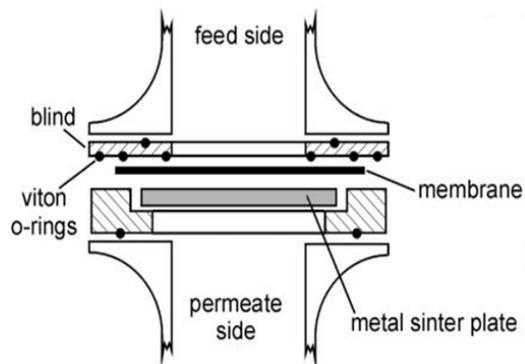


Diffusion and Permeability



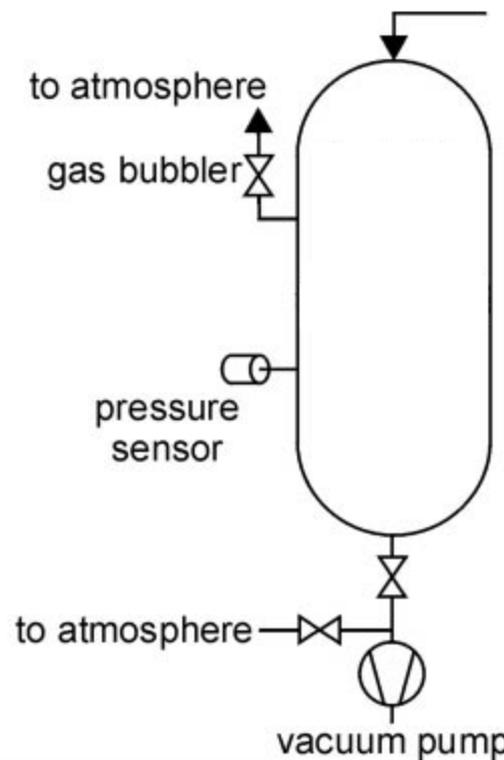
Permeance

■ Membrane Style



■ Column Style

SI Units: $\frac{\text{mol}}{\text{m}^2 \text{ s Pa}}$



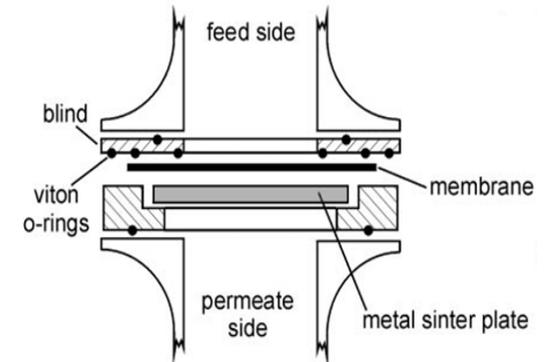
Permeance Measurements

■ Time-lag method

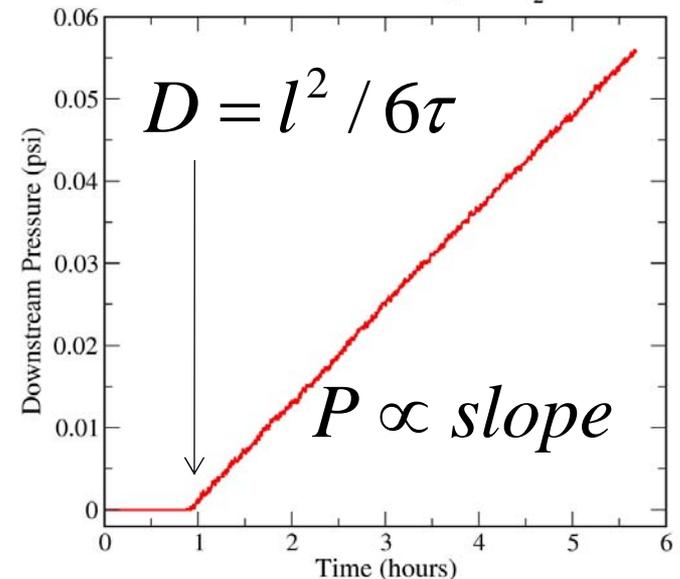
- Diffusion Coefficients (D)
- Permeance (P)
 - Gas flux per unit area per unit pressure

$$\left(\frac{\text{mol}}{\text{s}}\right) \cdot \left(\frac{1}{\text{m}^2}\right) \cdot \left(\frac{1}{\text{Pa}}\right)$$

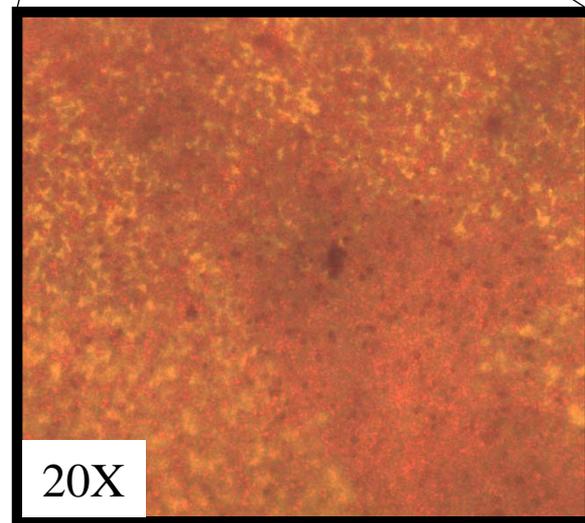
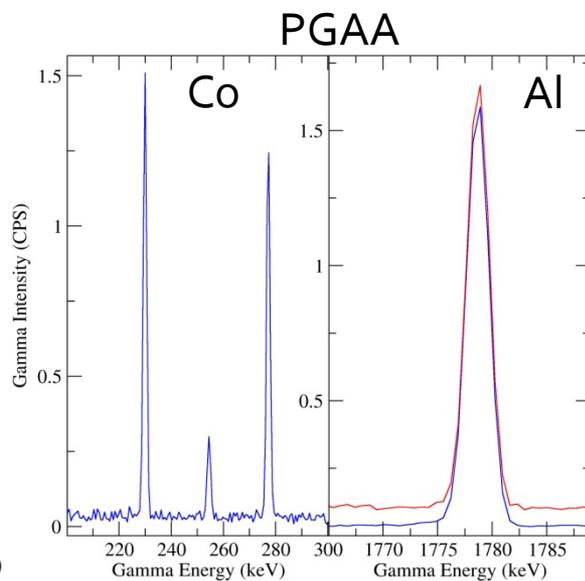
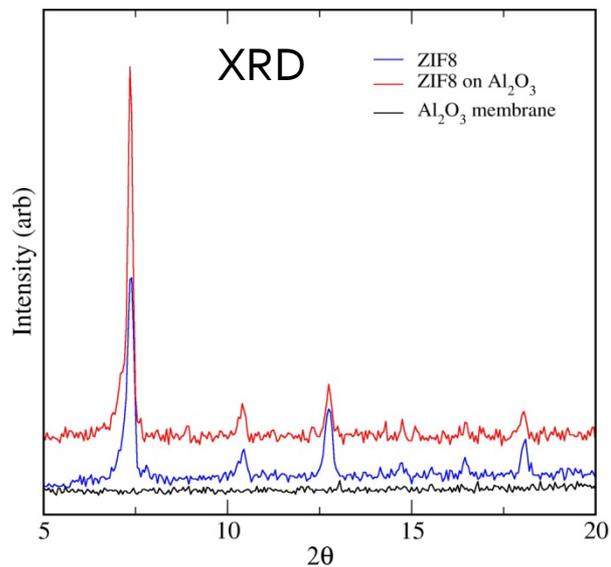
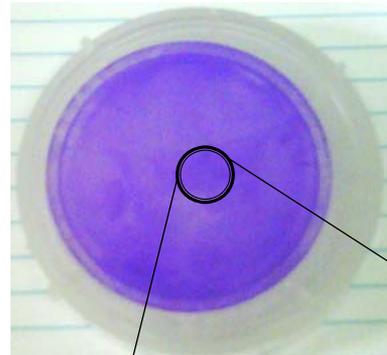
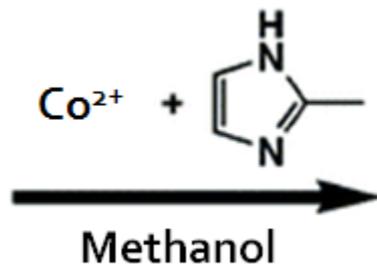
- Permeability = P *thickness
- Selectivity derived from measurements of individual permeances
- $S = P_1/P_2$



Nb membrane, 31psi CO₂



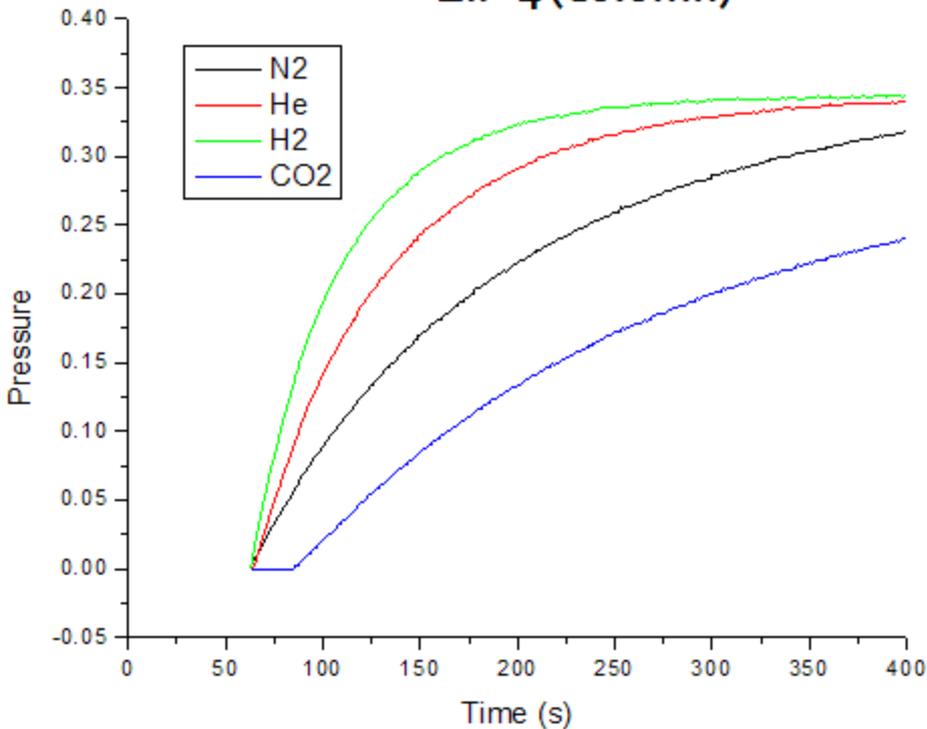
Membrane Synthesis



$\sim 1.7\text{mg ZIF-8/cm}^2$

Permeance Data - Column

ZIF-4 (Column)



Gas	Diffusion Coefficient (m ² s ⁻¹)	Permeance (mol s ⁻¹ m ⁻² Pa ⁻¹)
N ₂	5.21 × 10 ⁻⁵	1.17 × 10 ⁻⁵
H ₂	3.472 × 10 ⁻⁵	3.46 × 10 ⁻⁵
He	3.472 × 10 ⁻⁵	2.23 × 10 ⁻⁵
CO ₂	4.53 × 10 ⁻⁶	1.02 × 10 ⁻⁵

$$\text{Selectivity} = S = P_1 / P_2$$

CO₂/N₂ Selectivity

• Permeance = 1.14

• IAST = 1.30

$$P = \frac{dp}{dt} \frac{V}{RT\Delta P} = \frac{d}{dt} \frac{P_B}{P_T - P_B} \frac{V}{RTA}$$

Conclusion

- Adsorption, Selectivity, Permeance
- ZIF-4 and MOF-74 more selective for CO₂ than others studied
- Ground-level data for CO₂ project
- Future improvements:
 - Mixed gas streams - need measurement system downstream to distinguish individual gases
 - Temperature control for the sample
 - Modify membrane holder

Acknowledgments

- **Jason Simmons** 
- Center for High Resolution Neutron Scattering 
- NIST American Recovery and Reinvestment Act Measurement Science and Engineering Fellowship Program (NIST-ARRA)

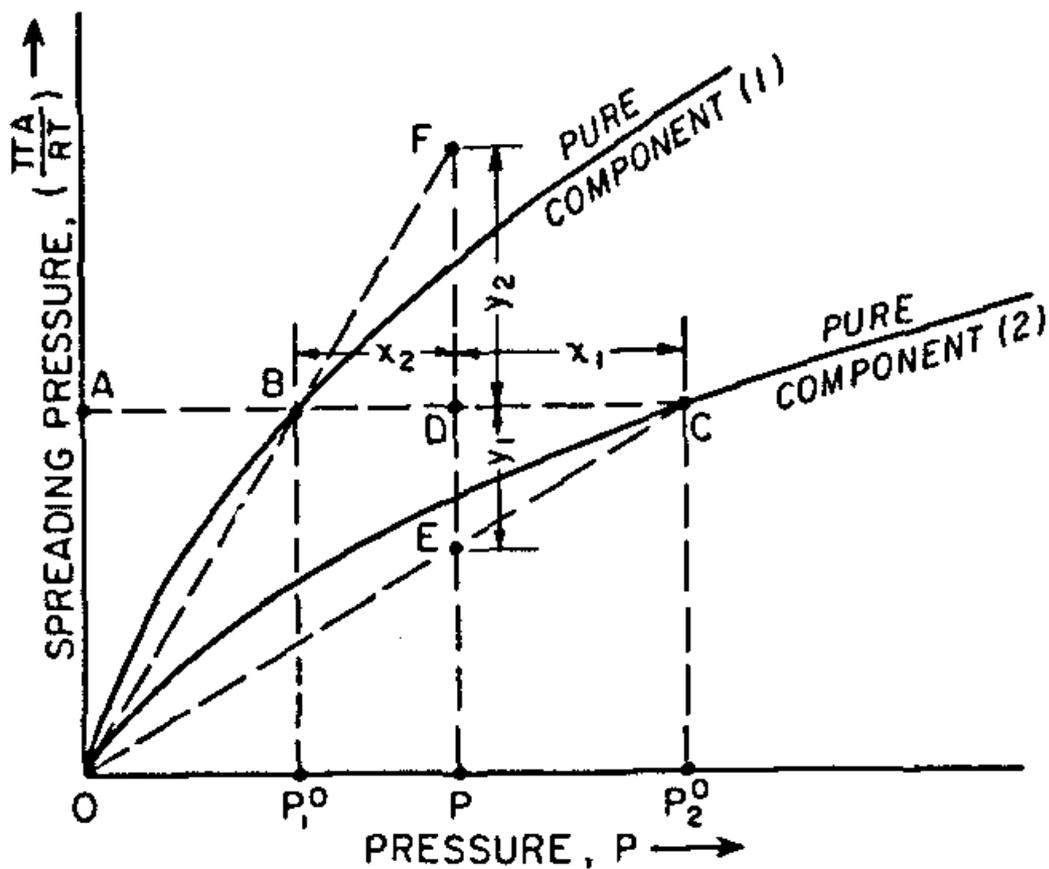
The End.

Extra Slides

Assumptions of the IAST

- The adsorbent is thermodynamically inert
- The adsorbent has a universal, temperature-invariant area
- The Gibbs definition of adsorption applies (surface excess)

IAST



$$\pi_1^{\circ} = \psi_1(P_1^{\circ})$$

$$\pi_2^{\circ} = \psi_2(P_2^{\circ})$$

$$Py_1 = P_1^{\circ}x_1$$

$$Py_2 = P_2^{\circ}x_2$$

$$\pi_1^{\circ} = \pi_2^{\circ}$$

$$x_1 + x_2 = 1$$

$$y_1 + y_2 = 1$$

Fig. 1. Calculation of mixture adsorption equilibria from pure component spreading pressures.

NOTATION

- A = specific area of adsorbent
 a = specific area per mole of adsorbate
 $f_i^\circ(\pi)$ = equilibrium fugacity for pure i corresponding to spreading pressure π
 F_i = adsorption isotherm function for pure component i
 G = Gibbs free energy of adsorbed phase
 g = molar Gibbs free energy of adsorbed phase
 h = molar enthalpy
 K_i = Henry's law constant for adsorption of pure i
 n_i = number of moles of component i in adsorbed phase per unit mass of adsorbent
 n_t = total number of moles in adsorbed phase per unit mass of adsorbent
 $P_i^\circ(\pi)$ = equilibrium pressure for pure i corresponding to spreading pressure π
 P = total pressure
 R = gas constant
 S = entropy of adsorbed phase
 $s_{1,2}$ = selectivity coefficient for component 1 relative to component 2
 T = absolute temperature
 t = dummy variable
 U = internal energy of adsorbed phase
 w = any extensive molar property
 x_i = mole fraction of component i in adsorbed phase
 y_i = mole fraction of component i in gas phase

Greek Letters

- $\alpha_{1,2}$ = volatility of component 1 relative to component 2
 γ_i = activity coefficient of component i in adsorbed phase
 μ_i = chemical potential of component i
 π = spreading pressure
 ϕ_i = vapor-phase fugacity coefficient of component i
 ψ = function

Superscripts

- m = change of property upon mixing at constant T and π
 o = standard state

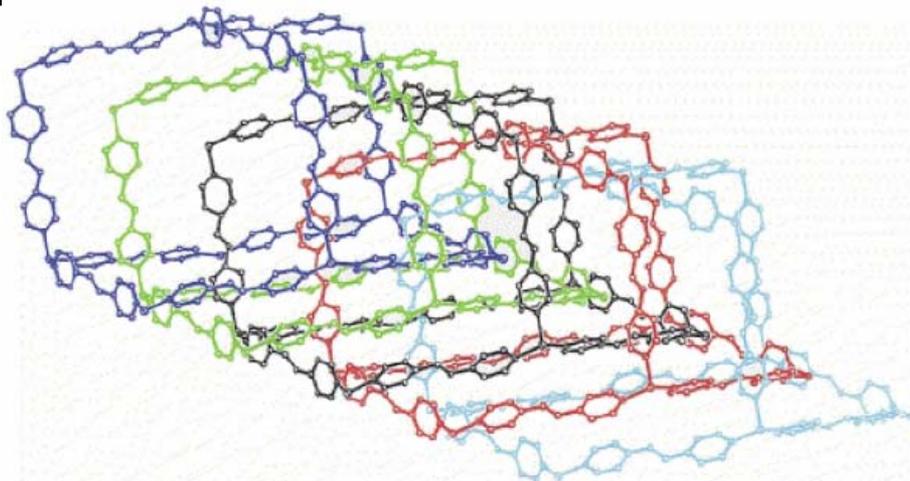
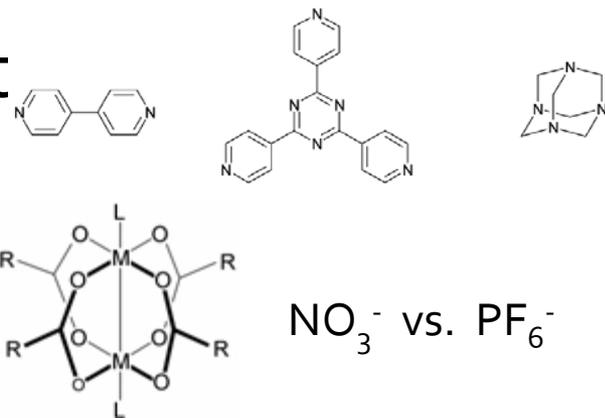
Subscripts

- i = component i

Problems in Synthesis

- Prediction of Network Geomet

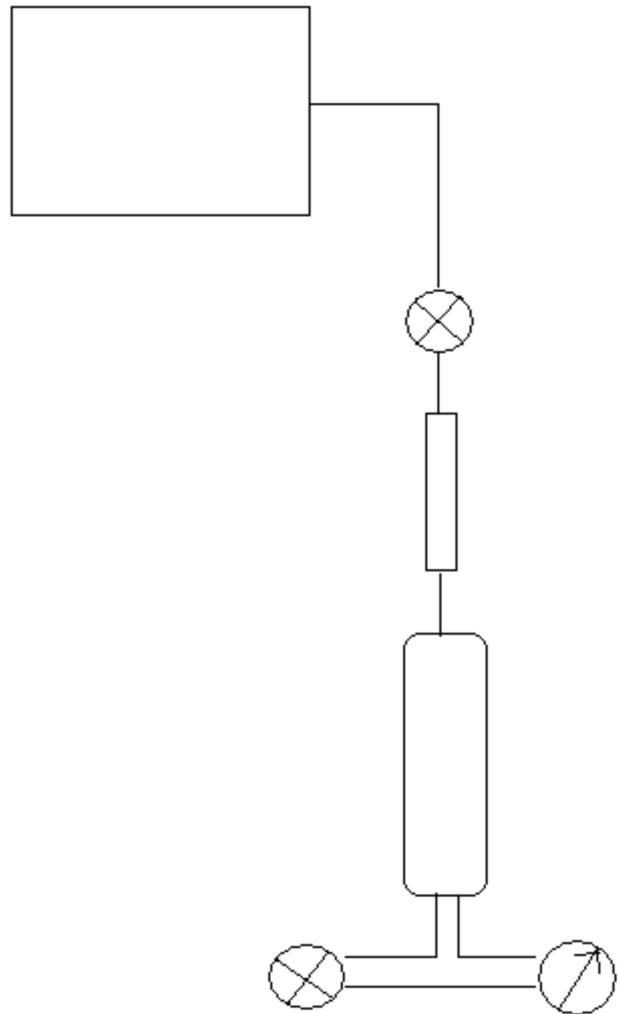
- Rigid Ligands
- Recurring Coordination Motifs
- Structure Directing Agents
- Effect of the Anion



Interpenetration

- Porosity

Equation	$y = a + b*x$		
Weight	No Weightin		
Residual Sum of Squares	1.96417E-4		
Adj. R-Square	0.99591		
		Value	Standard Error
B	Intercept	-0.12303	0.00183
	Slope	0.0021	1.90463E-5

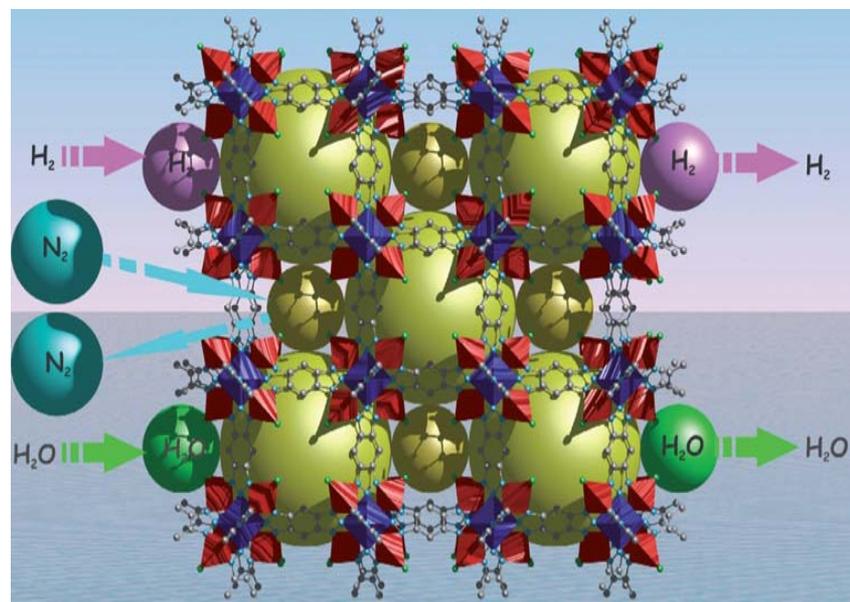


Selective Gas Adsorption

- Molecular Sieving Effect
 - Size exclusion
- Thermodynamic Equilibrium Effect
 - Packing interactions
- Kinetic Effect
 - Rates of diffusion
- Quantum Sieving Effect
 - Diffusion in micropores

Kinetic Diameters

He	2.6 Å
CO ₂	3.3 Å
O ₂	3.46 Å
N ₂	3.64 Å
CH ₄	3.8 Å



Selectivity: ZIF-8

