**CO₂ Gas Mixture**
- Traditional combustion (coal)
- NGCC
- IGCC
- Oxyfuel
- Direct air capture

**Capture processes**

**Absorption**
- Design parameters
  - Column height
  - Column width
  - # Columns
- Solvent properties
  - CO₂ solubility
  - Diffusion (CO₂/base)
  - Reaction kinetics
- Work requirements
  - Gas Blowing
  - Solvent pumping
  - Heat of Regeneration

**Adsorption**
- Design parameters
  - MTZ bed height
  - Column width
  - # Columns
- Sorbent properties
  - Pore size
  - Capacity
  - Phys/chem Diffusion
- Work requirements
  - Pressure difference
  - Sorbent loading
  - Binding strength

**Membrane**
- Design parameters
  - Surface area
  - Thickness
- Memb properties
  - Solubility
  - Diffusion
  - Permeability
  - Selectivity
- Work requirements
  - Pressure difference
  - Compression
  - Stage cut

**2nd law:** \[ \eta = \frac{W_{\text{min}}}{W_{\text{real}}} \]

**Note:** time scales (rates of mass transfer) are not represented in the work calculation
Coal to Electricity

- Furnace is pre-heated by combustion of auxiliary fuel such as natural gas or oil;
- Pulverized coal powder is blown with air into a combustion chamber (boiler or furnace) through a series of nozzles;
- Heat is transferred from hot combustion products to water circulating in tubes along the boiler walls, producing superheated steam, which is the working fluid for the steam turbines;
- Energy from the hot and pressurized steam is extracted in steam turbines that then transmit the energy to electric generators;
- The electric generators convert the shaft work of the turbines into alternating current electricity;
- Pumps are used to return the condensed water to the boiler, where the cycle is then repeated; and
- Pollution control devices are also in place for NOx, SOx, PM, and Hg.

*Images courtesy of Y. Liu, SU, 2009
Typical Coal-Fired Power Plant
Pulverized Coal Combustion (PCC)

- Oxidizing environment
- Mix of CO$_2$ and N$_2$
- $\sim 12$ mol. % CO$_2$

Fig. 1. Illustrative flowsheet for PCC (post-combustion capture) process, with additional unit operations for carbon capture shown bold.

Integrated Gasification Combined Cycle (IGCC)

- Reducing environment
- Mix of CO\(_2\) and H\(_2\)
- ~ 40 mol. % CO\(_2\)

Fig. 2. Illustrative flowsheet for IGCC (pre-combustion capture) process, with additional unit operations for carbon capture shown bold.

Oxy-fuel Combustion

Mostly CO\textsubscript{2}/H\textsubscript{2}O, easier separation

- Oxidizing environment
- Mix of CO\textsubscript{2} and H\textsubscript{2}O
- high % CO\textsubscript{2}

Fig. 3. Illustrative flowsheet for oxy-fuel (Oxyf) process, with additional unit operations for carbon capture shown bold.

Roadmap

• Concentration of CO$_2$ in a given gas mixture dictates the energy required for separation
• The energy required for separation only partially dictates the cost and subsequent feasibility of a given separation process
CO₂ Gas Mixture
- Traditional combustion (coal)
  - NGCC
  - IGCC
  - Oxyfuel
- Direct air capture

% Capture
% Purity

Thermodynamic minimum work

Absorption
- Design parameters
  - Column height
  - Column width
  - # Columns

Solvent properties
- CO₂ solubility
- Diffusion (CO₂/base)
- Reaction kinetics

Work requirements
- Gas Blowing
- Solvent pumping
- Heat of Regeneration

Adsorption
- Design parameters
  - MTZ bed height
  - Column width
  - # Columns

Sorbent properties
- Pore size
- Capacity
- Phys/chem Diffusion

Work requirements
- Pressure difference
- Sorbent loading
- Binding strength

Membrane
- Design parameters
  - Surface area
  - Thickness

Memb properties
- Solubility
- Diffusion
- Permeability
- Selectivity

Work requirements
- Pressure difference
- Compression
- Stage cut

Real work

2nd law: \[ \eta = \frac{W_{\text{min}}}{W_{\text{real}}} \]

Note: time scales (rates of mass transfer) are not represented in the work calculation
Minimum Work for Separation
combined first and second laws

\[ W_{\text{min}} = RT \left[ n_B^{\text{CO}_2} \ln(y_B^{\text{CO}_2}) + n_B^{\text{B-CO}_2} \ln(y_B^{\text{B-CO}_2}) \right] + RT \left[ n_C^{\text{CO}_2} \ln(y_C^{\text{CO}_2}) + n_C^{\text{C-CO}_2} \ln(y_C^{\text{C-CO}_2}) \right] \\
- RT \left[ n_A^{\text{CO}_2} \ln(y_A^{\text{CO}_2}) + n_A^{\text{A-CO}_2} \ln(y_A^{\text{A-CO}_2}) \right] \]
Minimum Work for Separation

CO₂ in air (380 – 580 ppm)

T = 298K, T = 338K

CO₂ in NGCC (5 – 8%)
CO₂ in PCC (10 – 15%)
CO₂ in IGCC (40 – 60%)

Work (kJ/mol CO₂)
Mole Fraction of CO₂
Sherwood Plot for Flue Gas Scrubbing

*Calculations carried out using IECM, all cases assume 500-MW plant burning Appalachian bituminous, NGCC (477-MW) O&M + annualized capital costs are included in the cost estimates*
## Cost and Scale

<table>
<thead>
<tr>
<th>Process</th>
<th>Price [$/kg]</th>
<th>Concentration [mole fraction]</th>
<th>Emissions [kg/day]</th>
<th>Cost [1000s $/day]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_2)-PCC</td>
<td>0.045</td>
<td>0.121</td>
<td>8.59 \times 10^6</td>
<td>392</td>
</tr>
<tr>
<td>CO(_2)-NGCC</td>
<td>0.059</td>
<td>0.0373</td>
<td>3.01 \times 10^6</td>
<td>178</td>
</tr>
<tr>
<td>SO(_x) (MS)</td>
<td>0.66</td>
<td>0.00127</td>
<td>8.94 \times 10^4</td>
<td>59.6</td>
</tr>
<tr>
<td>SO(_x) (LS)</td>
<td>2.1</td>
<td>0.000399 (399 ppm)</td>
<td>2.32 \times 10^4</td>
<td>50.4</td>
</tr>
<tr>
<td>NO(_x)</td>
<td>1.1</td>
<td>0.000387 (387 ppm)</td>
<td>1.11 \times 10^4</td>
<td>12.5</td>
</tr>
<tr>
<td>Hg</td>
<td>22000</td>
<td>5 \times 10^{-9} (ppb)</td>
<td>0.951</td>
<td>21.6</td>
</tr>
</tbody>
</table>

“the recovery of potentially valuable solutes from dilute solution is dominated by the costs of processing large masses of unwanted materials.”

- Edwin Lightfoot

---

2\textsuperscript{nd}-Law Efficiency Drops with Concentration

*Manuscript in preparation in collaboration w/ Kurt House, et al.
Second Law Efficiency

• The second law efficiency or the exergy (maximum work possible) efficiency is used to compare the efficiency of a real process to a corresponding ideal process

\[ \eta_{2nd} = \frac{W_{\text{real}}}{W_{\text{ideal}}} \]

• The second law efficiency or the exergy efficiency (or effectiveness) is used to compare the efficiency of a cycle to a corresponding ideal cycle
How to Increase the 2\textsuperscript{nd}-Law Efficiency?

Taking a closer look at absorption via MEA as an example:

1. Regeneration
2. Compression
3. Blower/Fan
4. Pumping

Can we establish targets based upon scientific limits?
Should we reconsider the way in which we convert coal to energy?
Roadmap

- Operating vs Capital costs
- Where does minimum energy fit in?
- How should cost of CO$_2$ captured be defined?
CO₂ Gas Mixture
Traditional combustion (coal)
NGCC
IGCC
Oxyfuel
Direct air capture

Capture processes

Absorption
- Design parameters:
  - Column height
  - Column width
  - # Columns
- Solvent properties:
  - CO₂ solubility
  - Diffusion (CO₂/base)
  - Reaction kinetics
- Work requirements:
  - Gas Blowing
  - Solvent pumping
  - Heat of Regeneration

Adsorption
- Design parameters:
  - MTZ bed height
  - Column width
  - # Columns
- Sorbent properties:
  - Pore size
  - Capacity
  - Phys/chem Diffusion
- Work requirements:
  - Pressure difference
  - Sorbent loading
  - Binding strength

Membrane
- Design parameters:
  - Surface area
  - Thickness
- Membrane properties:
  - Solubility
  - Diffusion
  - Permeability
  - Selectivity
- Work requirements:
  - Pressure difference
  - Compression
  - Stage cut

% Capture
% Purity

Thermodynamic minimum work

2nd law:
\[ \eta = \frac{W_{\text{min}}}{W_{\text{real}}} \]

Real work

Capital versus O&M
CO₂ Gas Mixture
Traditional combustion (coal)
NGCC
IGCC
Oxyfuel
Direct air capture

Capture processes

Absorption
Design parameters
• Column height
• Column width
• # Columns

Solvent properties
CO₂ solubility
Diffusion (CO₂/base)
Reaction kinetics

Work requirements
• Gas Blowing
• Solvent pumping
• Heat of Regeneration

Adsorption
Design parameters
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Design parameters
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• Permeability
• Selectivity

Work requirements
• Pressure difference
• Compression
• Stage cut

Real work

2nd law:
\[ \eta = \frac{W_{\text{min}}}{W_{\text{real}}} \]

Note: time scales (rates of mass transfer) are not represented in the work calculation
Gas absorber using a solvent regenerated by stripping (a) Absorber, (b) Stripper
Components of Absorption

Total Cost

Capital cost

% Capture
- Numbers of stages and tower height

Mass transfer and L/V ratio

Sorption rate

Physical sorption

Chemical sorption

Solubility

Diffusivity

Rate constant

Operating and maintenance costs

Energy requirements

Compression energy

Power: gas blowing, solvent pumping

Heat of regeneration

Water content

Solvent content and CO₂ loading

Binding strength

CO₂ product purity

Fluid properties
Mass Transfer of CO\(_2\) in Absorption

- Gas-phase CO\(_2\) diffusion
- CO\(_2\) concentration in the bulk gas is based upon the CO\(_2\) concentration in the gas mixture
- CO\(_2\) dissolution at the gas-liquid interface
- CO\(_2\) concentration at the interface is determined by Henry’s Law
- Liquid-phase CO\(_2\) diffusion
- Simplifying assumption is that bulk liquid-phase CO\(_2\) concentration is zero

---

Later – Rate of Absorption and what this entails!
Carbonate versus Carbamate

1. Dissolution of CO₂ (physical)
2. Bicarbonate formation
   - CO₂:amine = 1
   - Low heat of absorption
3. Carbamate formation
   - CO₂:amine = 0.5 (lower capacity)
   - High heat of absorption

Tertiary amine acts as a base catalyst, forming a H bond with water, weakening the OH bond and allowing for hydration of CO₂ to bicarbonate.
Special Case: Carbonic Anhydrase

- CA is a Zn-containing metalloenzyme
- Facilitates hydration and dehydration of CO$_2$
- Rate of reaction is up to 8 orders of magnitude faster than CO$_2$ binding in neutral water w/out catalyst
Rate of Absorption

- **Gas-phase:**
  \[
  J_{G,CO_2} = c_{CO_2}^G G - D_{G,CO_2} \left| \frac{dc_{CO_2}}{dz} \right|_i = c_{CO_2}^G G - \frac{D_{G,CO_2}}{\delta} \left( c_{G^\infty,CO_2} - c_{i,CO_2} \right)
  \]
  \[
  = c_{CO_2}^G G - k_{G,CO_2} \left( c_{G^\infty,CO_2} - c_{i,CO_2} \right)
  \]

- **Liquid-phase:**
  \[
  J_{L,CO_2} = c_{CO_2}^L L - D_{L,CO_2} \left| \frac{dc_{CO_2}}{dz} \right|_i = c_{CO_2}^L L - \frac{D_{L,CO_2}}{\delta} \left( c_{L^\infty,CO_2} - c_{i,CO_2} \right)
  \]
  \[
  = c_{CO_2}^L L - k_{L,CO_2} \left( c_{L^\infty,CO_2} - c_{i,CO_2} \right)
  \]

J is the overall flux including bulk and diffusive terms, δ is the film thickness (gas or liquid), \(c^\infty\) is the concentration of the bulk (gas or liquid), i represents the interface, and k is the mass-transfer coefficient.
Gas and Liquid Diffusion Films

Bulk Gas

Gas Film

Gas-liquid interface

Liquid Film

Bulk Liquid
## Potentially Tunable Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Name</th>
<th>Typical Units</th>
<th>Likely Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D$</td>
<td>Gas diffusivity</td>
<td>cm²/s</td>
<td>0.1 – 1.0</td>
</tr>
<tr>
<td>$H_{CO_2}$</td>
<td>Henry’s law constant</td>
<td>atm</td>
<td>20 – 1700</td>
</tr>
<tr>
<td>$D_{L,CO_2}$</td>
<td>Liquid diffusivity</td>
<td>cm²/s</td>
<td>(0.5 – 2.0) × 10⁻³</td>
</tr>
<tr>
<td>$D_B$</td>
<td>Liquid diffusivity of absorbent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_2$</td>
<td>Reaction rate constant</td>
<td>L/mol·s</td>
<td>$6.7 \times 10^{-4} – 1.2 \times 10^{5}$</td>
</tr>
<tr>
<td>$c_B$</td>
<td>Bulk concentration of absorbent</td>
<td>mol/L</td>
<td>0.1 – 8⁻</td>
</tr>
<tr>
<td>$k_{L,CO_2}$</td>
<td>Liquid-phase mass-transfer</td>
<td>cm/s</td>
<td>$10^{-2}$</td>
</tr>
<tr>
<td>$c_{i,CO_2}$</td>
<td>Concentration of CO₂</td>
<td>mol/L</td>
<td>set by $p_{CO_2}$ and $H_{CO_2}$</td>
</tr>
<tr>
<td>$D_B/D_{L,CO_2}$</td>
<td>Diffusivity ratio</td>
<td></td>
<td>0.2 – 2.0</td>
</tr>
</tbody>
</table>

†depending on the corrosive nature, typically less than 1.0 mol/L
# Absorption-Related Mass-Transfer Correlations

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Correlation</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid in packed-bed</td>
<td>$k \left( \frac{1}{ug} \right)^{1/3} = 0.0051 \left( \frac{u}{ua} \right)^{0.67} \left( \frac{D}{v} \right)^{0.5} (ad)^{0.4}$</td>
<td>Known as best available correlation for liquids</td>
</tr>
<tr>
<td></td>
<td>$kl \frac{D}{v} = 25 \left( \frac{lu}{v} \right)^{0.45} \left( \frac{D}{v} \right)^{0.5}$</td>
<td>Classical result and widely referenced</td>
</tr>
<tr>
<td>Gas bubbles in stirred tank</td>
<td>$kl \frac{D}{v} = 0.13 \left( \frac{(P/V)l^4}{\rho v^3} \right)^{1/4} \left( \frac{v}{D} \right)^{1/3}$</td>
<td>$k$ is not dependent on bubble size</td>
</tr>
<tr>
<td>Gas bubbles in unstirred tank</td>
<td>$kl \frac{D}{v} = 0.31 \left( \frac{l^3 g \Delta \rho / \rho}{v^2} \right) \left( \frac{v}{D} \right)^{1/3}$</td>
<td>$\Delta \rho$ = density difference between bubble and fluid</td>
</tr>
<tr>
<td>Falling films</td>
<td>$kz \frac{D}{v} = 0.69 \left( \frac{zu}{D} \right)^{0.5}$</td>
<td>$z$ = position along film</td>
</tr>
</tbody>
</table>

Notes: $a$ = packing area per bed volume; $l$ = characteristic length (or bubble or drop diameter); $\varepsilon$ = bed voidage; $P/V$ = stirrer power per volume; $u$ = superficial velocity (or drop velocity)
Choosing an Appropriate Solvent

- high CO$_2$ capacity
- fast kinetics with CO$_2$
- low volatility
- low viscosity
- nontoxic, nonflammable, and noncorrosive
- high thermal stability
- resistance to oxidation
- Examples include amines, carbonates, and ammonia
Real Work: Fan and Blower Power

- Fans and blowers:
  - Fans operate near atm P w/ $\Delta P < 15$ kPa
  - Efficiency, $\varepsilon$, gas density, $\rho$, and pressure drop, $\Delta P$, fan power is:

$$Power = \frac{dw_f}{dt} = \frac{\dot{m}\Delta p}{\rho \cdot \varepsilon}$$

  - Blowers handle $3 < \Delta P < 500$ kPa
  - For adiabatic and reversible compression of an ideal gas, blowing power is:

$$Power = \frac{dw_b}{dt} = \frac{\dot{m}RT_1 k}{M (k - 1) \varepsilon} \left[ \left( \frac{p_2}{p_1} \right)^{(k - 1)/k} - 1 \right]$$

$T_1$ is the initial gas temperature, $p_1$ and $p_2$ are the initial and final gas pressures, and $k$ is the ratio of specific heats (Appendix B of text)
- Efficiencies can range from 65 - 85%
Real Work: Solvent Pumping Power

- Pumps for solvent pumping:
  - To cause liquid to flow work must be expended; a pump can assist in overcoming pressure drop associated with solvent friction in a column and can also assist in raising the solvent to a higher elevation.
  - Work is a function of the change in pressure and volumetric flow rate, $Q$:

$$\text{Power} = \frac{dw_p}{dt} = \frac{Q \Delta p}{\varepsilon_i \varepsilon_d}$$

  - Intrinsic efficiencies, $\varepsilon_i$, range from 40 to 85%, while drive efficiency, $\varepsilon_d$, can be approximated as 85%.
Real Work: Heat of Regeneration

Heat required for regeneration:

- lean loading: 0.2 mol CO$_2$/mol MEA
- rich loading: 0.4 mol CO$_2$/mol MEA
- heat up solvent, e.g., heat capacity of 30 wt.% MEA w/ 0.4 mol bound CO$_2$ = 3.418 J/g·K
- mass of solution = 0.4 mol CO$_2$ + 7.9 mol H$_2$O + 1 mol MEA
- 40 to 120 °C is ~ 60.5 kJ to just heat up the water
- Additional 16.9 kJ/mol MEA to break the CO$_2$ bond (~ 84 kJ/mol CO$_2$)
- For regeneration of 0.2 mol CO$_2$/1 mol MEA:
  - (60.5 + 16.9) kJ/mol MEA x 1.0 mol MEA/0.2 mol CO$_2$ = 387 kJ/mol CO$_2$
  - IECM (Rubin et al.) estimates ~ 39 kJ/mol; Rochelle estimates ~ 30 kJ/mol
- Why the gap?
  - Heat exchange from the absorption process (water is an excellent heat transfer fluid)
  - Heat exchange from multiple cycles
Real Work: Compression

- Compression of CO\textsubscript{2} to 10 MPa is recommended for pipeline transport
- Adiabatic single-stage compression power can be calculated for an ideal gas by:

\[ P_{ad} = \frac{mRT}{M} \frac{k}{k-1} \left( r^{(k-1)/k} - 1 \right) \]

Such that \( m \) is the mass flow rate, \( T \) is the gas temperature, \( r \) is the compression ratio, i.e., \( p_2/p_1 \), \( k \) is the ratio of heat capacities (i.e., \( C_v/C_p \)), and \( M \) is the molecular weight of the gas

- Compression of CO\textsubscript{2} from 1 atm (0.101 MPa) to 10 Mpa \( \sim 20 \) kJ/mol CO\textsubscript{2}
- Rochelle et al. report significantly lower compression (\( \sim 10 \) kJ/mol CO\textsubscript{2}) requirements due to novel stripping schemes that incorporate gas compression within the process
- IECM (Rubin et al.) report compression work \( \sim 23 \) kJ/mol CO\textsubscript{2}
Real Work – Total

- Total real work required for CO₂ capture includes:
  - $W_{\text{fan}} + W_{\text{pump}} + W_{\text{regen}} + W_{\text{comp}}$

- On average, estimates for an amine-based absorption process (from IECM)
  - $W_{\text{fan}} \sim 7 \text{ kJ/mol CO₂}$
  - $W_{\text{pump}} \sim 0.5 \text{ kJ/mol CO₂}$
  - $W_{\text{regen}} \sim 39 \text{ kJ/mol CO₂}$
  - $W_{\text{comp}} \sim 23 \text{ kJ/mol CO₂} \ [1 \text{ atm} \rightarrow 10 \text{ MPa}]$
CO₂ Gas Mixture
- Traditional combustion (coal)
- NGCC
- IGCC
- Oxyfuel
- Direct air capture

Capture processes

Absorption
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  - Surface area
  - Thickness
- Membrane properties
  - Solubility
  - Diffusion
  - Permeability
  - Selectivity
- Work requirements
  - Pressure difference
  - Compression
  - Stage cut

Real work

Note: time scales (rates of mass transfer) are not represented in the work calculation

2nd law: \[ \eta = \frac{W_{\text{min}}}{W_{\text{real}}} \]
Outline of Adsorption Processes

Total Cost

- Capital cost
  - MTZ and bed height
    - Sorption rate
      - Physisorption or Chemisorption (Equilibrium)
        - Diffusion (Time)
          - Sorption capacity
            - % Capture
              - Sorption capacity
                - Sorbent properties: Micro, Meso and Macroporous, Tortuosity

- Operating and maintenance costs
  - Energy requirements
    - Compression energy
      - Pressure drop
        - Bed type: Moving vs Fixed
          - Heat of regeneration
            - Sorbent loading
              - Binding strength
                - CO₂ product purity
Physisorption versus Chemisorption

- When CO$_2$ is held loosely via weak intermolecular forces it’s termed physisorption, heat of adsorption $\sim 10 - 15$ kcal/mol
- When CO$_2$ is held via covalent bonds it’s termed chemisorption
- Most CO$_2$ adsorption mechanisms are physisorption due to the need for low heats of adsorption
- Heats of adsorption of zeolites and MOFs can actually be quite high (e.g., $\sim 50$ kcal/mol)
## Kinetic and Electrostatic Properties of Gases

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$^{15}$Kinetic Diameter (nm)</th>
<th>$^{16}$Dipole Moment (Debye)</th>
<th>$^{17}$Quadrupole Moment (10^{-40} Coulomb·m^2)</th>
<th>$^{16-17, 17^d}$Polarizability (10^{-24} cm^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>0.33</td>
<td>0</td>
<td>-13.71, -10.0</td>
<td>2.64, 2.91, 3.02</td>
</tr>
<tr>
<td>N₂</td>
<td>0.346</td>
<td>0</td>
<td>-4.91</td>
<td>0.78, 1.74</td>
</tr>
<tr>
<td>O₂</td>
<td>0.346</td>
<td>0</td>
<td>-1.33</td>
<td>1.57, 1.77</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.280</td>
<td>1.85</td>
<td>6.67</td>
<td>1.45, 1.48</td>
</tr>
<tr>
<td>SO₂</td>
<td>0.360</td>
<td>1.63</td>
<td>-14.6</td>
<td>3.72, 3.89, 4.28</td>
</tr>
<tr>
<td>NO</td>
<td>0.317</td>
<td>0.16</td>
<td>-6.00</td>
<td>1.7</td>
</tr>
<tr>
<td>NO₂</td>
<td>0.340</td>
<td>0.316</td>
<td>unknown</td>
<td>3.02</td>
</tr>
<tr>
<td>NH₃</td>
<td>0.260</td>
<td>1.47, 5.10</td>
<td>-7.39</td>
<td>2.22, 2.67, 2.81</td>
</tr>
<tr>
<td>HCl</td>
<td>0.346</td>
<td>1.11, 3.57</td>
<td>13.28</td>
<td>2.63, 2.94</td>
</tr>
<tr>
<td>CO</td>
<td>0.376</td>
<td>0.11, 0.37</td>
<td>-8.33, -6.92</td>
<td>1.95, 2.19</td>
</tr>
<tr>
<td>N₂O</td>
<td>0.317</td>
<td>0.16, 0.54</td>
<td>-12.02, -10.0</td>
<td>3.03, 3.32</td>
</tr>
<tr>
<td>Ar</td>
<td>0.340</td>
<td>0</td>
<td>0</td>
<td>1.64, 1.83</td>
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<tr>
<td>H₂</td>
<td>0.289</td>
<td>0</td>
<td>2.09, 2.2</td>
<td>0.81, 0.90</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.380</td>
<td>0</td>
<td>0</td>
<td>2.6</td>
</tr>
</tbody>
</table>
## Common Types of Sorbents

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Pore Diameter (nm)</th>
<th>Sorbent Density (kg/m³)</th>
<th>Sorbent Porosity</th>
<th>BET Surface Area (m²/g)</th>
<th>H₂O cap. Wt. %, 25 °C, 4.6 mmHg</th>
<th>CO₂ cap. Wt. %, 25 °C, 250 mmHg</th>
<th>Regeneration Temp, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Activated carbon</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Small pore</td>
<td>1-2.5</td>
<td>500-900</td>
<td>0.4-0.6</td>
<td>400-1200</td>
<td>1</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>Large pore</td>
<td>&gt; 3</td>
<td>600-800</td>
<td>-</td>
<td>200-600</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>Zeolites</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3A</td>
<td>0.3</td>
<td>670-740</td>
<td>0.2</td>
<td>700</td>
<td>20</td>
<td>-</td>
<td>&gt; 350</td>
</tr>
<tr>
<td>4A</td>
<td>0.4</td>
<td>660-720</td>
<td>0.3</td>
<td>700</td>
<td>23</td>
<td>13</td>
<td>120-350</td>
</tr>
<tr>
<td>5A</td>
<td>0.5</td>
<td>670-720</td>
<td>0.4</td>
<td>650</td>
<td>21</td>
<td>15</td>
<td>120-350</td>
</tr>
<tr>
<td>13X</td>
<td>0.8</td>
<td>610-710</td>
<td>0.5</td>
<td>600</td>
<td>25</td>
<td>16</td>
<td>120-350</td>
</tr>
<tr>
<td>Mordenite</td>
<td>0.3-0.4</td>
<td>720-800</td>
<td>0.25</td>
<td>700</td>
<td>9</td>
<td>6</td>
<td>-</td>
</tr>
<tr>
<td>Chabazite</td>
<td>0.4-0.5</td>
<td>640-720</td>
<td>0.35</td>
<td>650</td>
<td>16</td>
<td>12</td>
<td>-</td>
</tr>
<tr>
<td><strong>Silica gel</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Small pore</td>
<td>2.2-2.6</td>
<td>1000</td>
<td>0.47</td>
<td>800</td>
<td>11</td>
<td>3</td>
<td>130-280</td>
</tr>
<tr>
<td>Large pore</td>
<td>10-15</td>
<td>620</td>
<td>0.71</td>
<td>320</td>
<td>-</td>
<td>-</td>
<td>130-280</td>
</tr>
<tr>
<td><strong>Activated alumina</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-7.5</td>
<td>14a. 28</td>
<td>800</td>
<td>0.50</td>
<td>320</td>
<td>7</td>
<td>2</td>
<td>150-315</td>
</tr>
<tr>
<td><strong>MOFs</strong></td>
<td>0.4-2.4</td>
<td>200-1000</td>
<td>0.79-0.90</td>
<td>150-6200</td>
<td>9</td>
<td>4-14, 15</td>
<td>25-80</td>
</tr>
<tr>
<td><strong>Ion exchange resins</strong></td>
<td>&lt;1-12</td>
<td>^a1100, ^b1270</td>
<td>0.2-0.5</td>
<td>15-120</td>
<td>-</td>
<td>-</td>
<td>60</td>
</tr>
<tr>
<td><strong>Hollow fibers</strong></td>
<td>2.5-11</td>
<td>1250</td>
<td>0.3-0.8</td>
<td>450-1100</td>
<td>-</td>
<td>-</td>
<td>100-150</td>
</tr>
<tr>
<td><strong>CMS</strong></td>
<td>0.3-0.9</td>
<td>640-1000</td>
<td>0.5</td>
<td>400</td>
<td>&gt;20</td>
<td>1.2-2.5</td>
<td>100-200</td>
</tr>
<tr>
<td><strong>Amine-based</strong></td>
<td>8-40</td>
<td>1000-1500</td>
<td>5-500</td>
<td>-</td>
<td>5-14</td>
<td>80-120</td>
<td></td>
</tr>
<tr>
<td><strong>Hydrotalcites</strong></td>
<td>2-20</td>
<td>150-550</td>
<td>0.15-0.5</td>
<td>16-290</td>
<td>-</td>
<td>-</td>
<td>120-400</td>
</tr>
<tr>
<td><strong>Chemisorbents</strong></td>
<td>0.2-20</td>
<td>2000</td>
<td>250-1250</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>^c700-920</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>d150-500</td>
</tr>
</tbody>
</table>

^a^ Data for 1100, ^b^ Data for 1270.
Zeolite Framework
Zeolite Properties

• Aluminum prefers to bond 3 ways, so will have a charge of -1 when tetrahedrally bonded.
• Cations (positive charges) are used to stabilize these charges
• Cations distribute themselves in a way to minimize the free energy of the system
• How do zeolites work to separate N\textsubscript{2} from O\textsubscript{2}?
  – They actually prefer to adsorb N\textsubscript{2}
  – The interaction energy bet/ ions and N\textsubscript{2} are much stronger than ions and O\textsubscript{2}
    • O\textsubscript{2}-Na\textsuperscript{+} (20 kJ/mol); N\textsubscript{2}-Na\textsuperscript{+} (36 kJ/mol)
    • O\textsubscript{2}-Li\textsuperscript{+} (32 kJ/mol); N\textsubscript{2}-Li\textsuperscript{+} (51 kJ/mol)
  – N\textsubscript{2} has a higher quadrupole moment than O\textsubscript{2}
  – Adsorption is dependent upon the interaction energy bet/ an adsorbate and a cation of a zeolite and includes contributions from van der waals and electrostatic interactions. Electrostatic energies include induced dipoles, permanent dipoles and quadrupoles.
Building Blocks of Metal-Organic Frameworks

Diagram showing the combination of metal, organic linker, and resulting framework.
MOF Framework
Hollow-fiber Sorbents

(a) Sorbent particles
(b) Porous polymer matrix
Impermeable lumen layer

Adsorption
- CO₂
- Spent Water
- Water

Regeneration
- Spent Steam
- CO₂
- Steam
# Adsorption Cycles

<table>
<thead>
<tr>
<th>Process condition</th>
<th>Temperature Swing</th>
<th>Displacement Purge</th>
<th>PSA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorbate concentration in feed, &lt; 3%</td>
<td>yes</td>
<td>unlikely</td>
<td>unlikely</td>
</tr>
<tr>
<td>Adsorbate concentration in feed, 3-10%</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>Adsorbate concentration in feed, &gt; 10%</td>
<td>no</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>High product purity required</td>
<td>yes</td>
<td>yes</td>
<td>possible</td>
</tr>
<tr>
<td>Thermal regeneration required</td>
<td>yes</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>Difficult adsorbate separation</td>
<td>possible</td>
<td>unlikely</td>
<td>NA</td>
</tr>
</tbody>
</table>
Pressure Drop

• Ergun verified this eqn. for a variety of different shapes of packing material with varying packing densities; the first void space term accounts for the viscous loss component and the second for the KE loss component

\[
\frac{\Delta P}{L} = \frac{150\bar{V}_0 \mu}{\Phi_s^2 D_p^2} \frac{(1 - \varepsilon)^2}{\varepsilon^3} + \frac{1.75 \rho \bar{V}_0^2}{\Phi_s D_p} \frac{1 - \varepsilon}{\varepsilon^3}
\]

• It is important to note that a small change in \(\varepsilon\) results in a large change in \(\Delta P\)

• Typical numbers for calculations:
  – Void fractions for spheres, cylinders, and granular packings typically range from 0.3-0.6
  – Sphericity ranges from 0.6-0.95
Real Work: Overcoming Pressure Drop

• How much blower power is required to overcome the pressure drop in an adsorption system of a packed tower?

\[
Power = P_1V_1\left(\frac{k}{k-1}\right)\left[\left(\frac{P_2}{P_1}\right)^{(k-1)/k} - 1\right]
\]

• \(P\) is power in kilowatts, \(P_1\) is the inlet pressure, \(P_2\) is outlet pressure, \(V_1\) is the flow rate of gas, \(k\) is the ratio of specific heat (\(k=C_p/C_v\), where \(C_p\) and \(C_v\) are the heat capacity at constant pressure and volume, respectively)
  – Typical values for \(k = 1.4\) for air
CO₂ Gas Mixture
- Traditional combustion (coal)
- NGCC
- IGCC
- Oxyfuel
- Direct air capture

Capture processes

Absorption
Design parameters
- Column height
- Column width
- # Columns

Solvent properties
- CO₂ solubility
- Diffusion (CO₂/base)
- Reaction kinetics

Work requirements
- Gas Blowing
- Solvent pumping
- Heat of Regeneration

Adsorption
Design parameters
- MTZ bed height
- Column width
- # Columns

Sorbent properties
- Pore size
- Capacity
- Phys/chem
- Diffusion

Work requirements
- Pressure difference
- Sorbent loading
- Binding strength

Membrane
Design parameters
- Surface area
- Thickness

Memb properties
- Solubility
- Diffusion
- Permeability
- Selectivity

Work requirements
- Pressure difference
- Compression
- Stage cut

Real work

2nd law:
\[ \eta = \frac{W_{\text{min}}}{W_{\text{real}}} \]

Note: time scales (rates of mass transfer) are not represented in the work calculation
Outline of Membrane Processes

Total Cost

Capital cost

Membrane surface area

Membrane flux

Permeance

Permeability

Solubility

Diffusion

Operating and maintenance costs

Energy requirements

Compression energy (pressure ratio)

Permeate mole fraction (purity)

Stage cut

% Capture

Selectivity
Membrane Separation Mechanisms

A. Porous Membranes

Convective flow through large pores. No separation occurs.

Knudsen diffusion through pores. Pores with diameters less than the mean free path of the gas molecules allow lighter molecules to preferentially diffuse through pore.

Molecular sieving. Large molecules are excluded from the pores by virtue of their size.

B. Solution-Diffusion Membranes

Gas dissolves into the membrane material and diffuses across it.
Gradients and Terminology
Permeability vs. Permeance

- Permeability vs Permeance

\[ J_A = \frac{D_A S_A (p_{A1} - p_{A2})}{z} = \bar{P}_A (p_{A1} - p_{A2}) \]

- \( J \) = flux; \( D \) = diffusivity, \( S \) = solubility, \( z \) = membrane thickness, and coefficient of pressure difference is the permeance
- Permeability is the product of diffusivity and solubility and is a property of the material
- Typical units of permeance are GPUs or standard ft\(^3\)/ft\(^2\) h atm
- Permeance is a property of a particular membrane
- Typical units of permeability are Barrers

\[ 1 \text{ Barrer} = 10^{-10} \frac{\text{cm}^3 \text{(STP)} \cdot \text{cm}}{\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}} \]
Selectivity

- Selectivity may be in terms of permeability, diffusivity, or solubility

\[ \alpha = \frac{P_A}{P_B} = \left( \frac{D_A}{D_B} \right) \left( \frac{S_A}{S_B} \right) \]

- In 1991, Lloyd M. Robeson quantified the trade-off between permeability and selectivity; displayed in terms of Robeson plots
Gas Separation Process Design

- CO₂ capture from natural gas
- Residue is purified CH₄ w/ permeate stream enriched in CO₂
- Note high feed and residue streams

<table>
<thead>
<tr>
<th>Stream</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Composition (mole %)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₄</td>
<td>93.0</td>
<td>98.0</td>
<td>63.4</td>
</tr>
<tr>
<td>CO₂</td>
<td>7.0</td>
<td>2.0</td>
<td>36.6</td>
</tr>
<tr>
<td><strong>Flow Rate (MMscf/d)</strong></td>
<td>20.00</td>
<td>17.11</td>
<td>2.89</td>
</tr>
<tr>
<td><strong>Pressure (psig)</strong></td>
<td>850</td>
<td>835</td>
<td>10</td>
</tr>
<tr>
<td><strong>Methane Recovery = 90.2%</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Flow Rate (SCFm)</strong></td>
<td>13890</td>
<td>11880</td>
<td>2007</td>
</tr>
</tbody>
</table>

*Figure 5. Single-stage membrane process for natural gas treating.*
Short-Cut Design Calculation

• Short-cut area calculation described by Hogsett and Mazur, Hydrocarbon Processing, 62, 52 (1983)

\[
Area = \frac{x_{1\text{perm}} Q_{\text{perm}}}{P_1 \left( \frac{P_{\text{feed}} x_{\text{log-mean}}}{l} - P_{\text{perm}} x_{1\text{perm}} \right)} \approx \frac{\text{permeate flow rate of 1}}{\text{flux of species 1}}
\]

where \( Q \) is volumetric flow rate, \( x \) is mole fraction, \( p \) is pressure

\[
P_1 \frac{l}{l}
\]

is permeance of species 1

\[
x_{\text{log-mean}} = \frac{x_{1\text{feed}} - x_{1\text{residue}}}{\ln \left( \frac{x_{1\text{feed}}}{x_{1\text{residue}}} \right)}
\]

• Using values from the previous slide and a \( \text{CO}_2 \) permeance of 5.5 \( \text{ft}^3 \) (STP)/(ft\(^2\) 100 psi hr), results in a membrane area of 31,500 \( \text{ft}^2 \)
Multi-Stage Processes

**Figure 8.** Two-stage gas separation membrane process for natural gas treating.

**Figure 9.** Multi-stage gas separation membrane process for natural gas treating.
Membrane Module Process Parameters

- Feed flow rate, temperature, and pressure
- Stream compositions
- Pressure ratio = permeate pressure/feed pressure ($R, \gamma$)
  - Baker uses $\phi = \text{feed/permeate pressures}$
- Stage cut = permeate flow rate/feed flow rate
- Component recovery = species flow rate in product stream/species flow rate in feed
  - Note: either permeate or residue can be the product. For natural gas purification, the residue stream containing the pipeline quality natural gas is the product
- Residue streams can be made arbitrary pure at a cost of higher membrane area and lower recovery
Local Permeate Concentration

Selectivity and pressure ratio effects on the local permeate concentration
Influence of Pressure Ratio

• Original Case:
  – 100 MSCFH natural gas
  – Feed pressure = 480 psia
  – Permeate pressure = 20 psia
  – ΔP = 460 psia
  – Pressure ratio, γ = 0.042
  – Feed CO₂ = 12%
  – Product CO₂ = 2%
  – Area required = 1,700 ft²

• New Case:
  – 100 MSCFH natural gas
  – Feed pressure = 1200 psia
  – Permeate pressure = 200 psia
  – ΔP = 1000 psia
  – Pressure ratio, γ = 0.17
  – Feed CO₂ = 12%
  – Product CO₂ = 2%
  – Area required = 7,800 ft²
### CO₂ Gas Mixture

Traditional combustion (coal)  
NGCC  
IGCC  
Oxyfuel  
Direct air capture

### Absorption

#### Design parameters
- Column height  
- Column width  
- # Columns

#### Solvent properties
- CO₂ solubility  
- Diffusion (CO₂/base)  
- Reaction kinetics

#### Work requirements
- Gas Blowing  
- Solvent pumping  
- Heat of Regeneration

### Adsorption

#### Design parameters
- MTZ bed height  
- Column width  
- # Columns

#### Sorbent properties
- Pore size  
- Capacity  
- Phys/chem Diffusion

#### Work requirements
- Pressure difference  
- Sorbent loading  
- Binding strength

### Membrane

#### Design parameters
- Surface area  
- Thickness

#### Memb properties
- Solubility  
- Diffusion  
- Permeability  
- Selectivity

#### Work requirements
- Pressure difference  
- Compression  
- Stage cut

### Work requirements
- Gas Blowing  
- Solvent pumping  
- Heat of Regeneration

### Thermodynamic minimum work

**2nd law:**  
\[ \eta = \frac{W_{\text{min}}}{W_{\text{real}}} \]

### Real work

**Note:** time scales (rates of mass transfer) are not represented in the work calculation