Energy Tutorial: Carbon Capture 101

Professor Jennifer Wilcox
Energy Resources Engineering Department
Global Climate and Energy Project
Stanford University

OCTOBER 5, 2011
**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

**2nd law:** \[ \frac{W_{\text{min}}}{W_{\text{real}}} \]
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 CO₂ and H₂
- ~ 40 mol. % CO₂

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

Oxy-fuel Combustion

- Oxidizing environment
- Mix of CO\(_2\) and H\(_2\)O
- high % CO\(_2\)

Fig. 3. Illustrative flowsheet for oxy-fuel (Oxyf) process, with additional unit operations for carbon capture shown bold.
Concentration of CO₂ 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.
Capture processes

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

**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

**Absorption**

**Adsorption**
- MTZ bed height
- Column width
- # Columns

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

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

**Membrane**
- Surface area
- Thickness

**Memb properties**
- Solubility
- Diffusion
- Permeability
- Selectivity

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

2\textsuperscript{nd} law: \( W = \frac{W_{\text{min}}}{W_{\text{real}}} \)

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

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

- CO$_2$ in air (380 – 580 ppm)
- CO$_2$ in NGCC (5 – 8%)
- CO$_2$ in PCC (10 – 15%)
- CO$_2$ in IGCC (40 – 60%)

Work (kJ/mol CO$_2$) vs. Mole Fraction of CO$_2$ for different temperatures T=298K and T=338K.
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>CO₂-PCC</td>
<td>0.045</td>
<td>0.121</td>
<td>$8.59 \times 10^6$</td>
<td>392</td>
</tr>
<tr>
<td>CO₂-NGCC</td>
<td>0.059</td>
<td>0.0373</td>
<td>$3.01 \times 10^6$</td>
<td>178</td>
</tr>
<tr>
<td>SOx (MS)</td>
<td>0.66</td>
<td>0.00127</td>
<td>$8.94 \times 10^4$</td>
<td>59.6</td>
</tr>
<tr>
<td>SOx (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>NOx</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.”\(^2\) - Edwin Lightfoot

\(^1\)These can change based upon coal-type burned and scrubbing methods; \(^2\)EN Lightfoot, MCM Cockrem, What Are Dilute Solutions, Sep. Sci. Technol., 22(2), 165, 1987.
2nd-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

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

• 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?
Capture processes

**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

**2nd law**: $$\frac{W_{\text{min}}}{W_{\text{real}}}$$

**Thermodynamic minimum work**

% Capture
% Purity

**Real work**
Capture processes

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

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

Absorption

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

Thermodynamic minimum work

% Capture
% Purity

Real work

2nd law:
\[ \frac{W_{\text{min}}}{W_{\text{real}}} \]
Gas absorber using a solvent regenerated by stripping (a) Absorber, (b) Stripper
Components of Absorption

Total Cost

- Capital cost
- Operating and maintenance costs

% Capture
- Numbers of stages and tower height
- Mass transfer and L/V ratio
- Sorption rate
- Physical sorption
- Chemical sorption

- Solubility
- Diffusivity
- Rate constant

Energy requirements
- Compression energy
- Power: gas blowing, solvent pumping
- Heat of regeneration
- Water content
- Solvent content and CO₂ loading
- Binding strength
- CO₂ product purity
Mass Transfer of CO₂ in Absorption

- Gas-phase CO₂ diffusion
- CO₂ concentration in the bulk gas is based upon the CO₂ concentration in the gas mixture
- CO₂ dissolution at the gas-liquid interface
- CO₂ concentration at the interface is determined by Henry’s Law
- Liquid-phase CO₂ diffusion
- Simplifying assumption is that bulk liquid-phase CO₂ concentration is zero

<table>
<thead>
<tr>
<th>Gas</th>
<th>Liquid Film</th>
<th>Liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step 1</td>
<td>Step 2</td>
<td>Step 3</td>
</tr>
<tr>
<td>CO₂</td>
<td>CO₂</td>
<td>CO₂ + B</td>
</tr>
<tr>
<td>diffusion</td>
<td>dissolution</td>
<td>diffusion</td>
</tr>
</tbody>
</table>

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 CO₂
- Rate of reaction is up to 8 orders of magnitude faster than CO₂ binding in neutral water w/out catalyst
Gas and Liquid Diffusion Films

Bulk Gas

Gas Film

Liquid Film

Bulk Liquid

Gas-liquid interface
Rate of Absorption

- **Gas-phase:**

\[
J_{G,CO_2} = c_{CO_2} G \quad D_{G,CO_2} \frac{dc_{CO_2}}{dz} \bigg|_i = c_{CO_2} G \quad D_{G,CO_2} \left( c_G,CO_2 \quad c_{i,CO_2} \right)
\]

\[
= c_{CO_2} G \quad k_{G,CO_2} \left( c_G,CO_2 \quad c_{i,CO_2} \right)
\]

- **Liquid-phase:**

\[
J_{L,CO_2} = c_{CO_2} L \quad D_{L,CO_2} \frac{dc_{CO_2}}{dz} \bigg|_i = c_{CO_2} L \quad D_{L,CO_2} \left( c_{i,CO_2} \quad c_L,CO_2 \right)
\]

\[
= c_{CO_2} L \quad k_{L,CO_2} \left( c_{i,CO_2} \quad c_L,CO_2 \right)
\]

\(J\) is the overall flux including bulk and diffusive terms, \(\delta\) 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.
Absorption (chemical)

• Irreversible 2\textsuperscript{nd}-order Reaction: \(CO_2 + B \xrightarrow{k_2} CO_2B\)
  – Assume that bulk CO\(_2\) concentration = 0 (i.e., \(c_\infty = 0\))

• Rate of Absorption = \(k_L c_{i,CO_2} E\)

• \(E =\) enhancement factor \(\rightarrow\) factor by which absorption rate is increased by rxn

• Enhancement factor is a function of:

\[ \sqrt{M} = \sqrt{D_{CO_2} k_2 c_B} \times \frac{k_L}{k_L} \quad \text{and} \quad E_i = 1 + \frac{D_B c_B}{2D_{CO_2} c_{i,CO_2}} \]

• \(E_i\) corresponds to instantaneous rxn

Danckwerts, Gas-Liquid Reactions, 1970
# Limiting Cases of the Film Model

In the case of the diffusion ratio between the base and CO$_2$ in the liquid deviates from unity, the Higbie Model is preferred

<table>
<thead>
<tr>
<th>Limiting Case</th>
<th>Enhancement Factor</th>
<th>Physical explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. $\sqrt{M} &gt; 10E_i$</td>
<td>$E = E_i$</td>
<td>Instantaneous reaction</td>
</tr>
<tr>
<td>2. $\sqrt{M} &lt; 1/2 E_i$</td>
<td>$E = \left( \frac{\sqrt{M}}{\tanh \sqrt{M}} \right)$</td>
<td>Pseudo first-order reaction</td>
</tr>
<tr>
<td>3. #2 satisfied and $\sqrt{M} &gt; 3$</td>
<td>$E = \sqrt{D_{L,CO_2} k_2 c_B}$</td>
<td>Fast pseudo first-order reaction</td>
</tr>
<tr>
<td>4. None of the above</td>
<td>Determine $E$ from Fig. 3.9</td>
<td></td>
</tr>
</tbody>
</table>

In the case of the diffusion ratio between the base and CO$_2$ in the liquid deviates from unity, the Higbie Model is preferred
Higbie Model

- $E_i$ is calculated from:

$$E_i = \sqrt{\frac{D_{L,CO_2}}{D_B}} + \frac{c_B}{zc_{i,CO_2}} \sqrt{\frac{D_B}{D_{L,CO_2}}}$$

Comparison of Model Absorption Rate Predictions for ↓HL; DR=2 Case

<table>
<thead>
<tr>
<th></th>
<th>Flue</th>
<th>Fuel</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Fast Pseudo-first Order</em></td>
<td>1.1(-4); 1.0(-6)</td>
<td>3.8(-4); 3.5(-6)</td>
</tr>
<tr>
<td><em>Film Model</em></td>
<td>5.2(-3); 1.0(-6)</td>
<td>7.9(-3); 3.4(-6)</td>
</tr>
<tr>
<td><em>Higbie Model</em></td>
<td>4.2(-3); 1.0(-6)</td>
<td>8.5(-3); 3.4(-6)</td>
</tr>
</tbody>
</table>
Enhancement Factor Predictions for Various Applications using the Film and Higbie Models

\[
E = \sqrt{\frac{M (E_i - E)}{E_i - 1}} \cdot \tanh \left( \sqrt{\frac{M (E_i - E)}{E_i - 1}} \right)
\]

<table>
<thead>
<tr>
<th>DR</th>
<th>Air</th>
<th>Flue</th>
<th>Fuel</th>
<th>Air</th>
<th>Flue</th>
<th>Fuel</th>
<th>E</th>
<th>E (from E_i (Film))</th>
<th>E (from E_i (Higbie))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1HL</td>
<td>4.6(5)</td>
<td>1.5(3)</td>
<td>4.5(2)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td>2600</td>
<td>520</td>
</tr>
<tr>
<td></td>
<td>9.3(5)</td>
<td>3.0(3)</td>
<td>9.1(2)</td>
<td>6.5(5)</td>
<td>2.1(3)</td>
<td>6.4(2)</td>
<td>34.6 (fast)</td>
<td>1600</td>
<td>720</td>
</tr>
<tr>
<td></td>
<td>3.9(7)</td>
<td>2.7(4)</td>
<td>8.2(3)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.316 (slow)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2HL</td>
<td>7.9(7)</td>
<td>5.5(4)</td>
<td>1.6(4)</td>
<td>5.5(7)</td>
<td>3.8(4)</td>
<td>1.1(4)</td>
<td></td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Rate of CO₂ Estimates for Various Applications using the Film and Higbie Models

\[
J_{L,CO₂} = c_{L,CO₂} \frac{mol}{cm²·s} \cdot E
\]

\[
\text{from } E_i (Film); \text{ [fast:slow]} \quad \text{from } E_i (Higbie); \text{ [fast:slow]}
\]

<table>
<thead>
<tr>
<th>DR</th>
<th>Air</th>
<th>Flue</th>
<th>Fuel</th>
<th>Air</th>
<th>Flue</th>
<th>Fuel</th>
<th>Fuel</th>
</tr>
</thead>
<tbody>
<tr>
<td>1HL</td>
<td>3.8(-7); 3.0(-9)</td>
<td>8.5(-3); 1.0(-6)</td>
<td>5.7(-3); 3.4(-6)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2HL</td>
<td>3.8(-7); 3.0(-9)</td>
<td>5.2(-3); 1.0(-6)</td>
<td>7.9(-3); 3.4(-6)</td>
<td>-</td>
<td>4.2(-3); 1.0(-6)</td>
<td>8.5(-3); 3.4(-6)</td>
<td>-</td>
</tr>
<tr>
<td>1HL</td>
<td>4.0(-9); 3.9(-11)</td>
<td>6.3(-7); 6.0(-9)</td>
<td>2.1(-5); 1.9(-7)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2HL</td>
<td>4.0(-9); 3.9(-11)</td>
<td>6.3(-7); 6.0(-9)</td>
<td>2.1(-5); 1.9(-7)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
## 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>cm$^2$/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>cm$^2$/s</td>
<td>$(0.5 – 2.0) \times 10^{-3}$</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>$6.7 \times 10^{-4} – 1.2 \times 10^8$</td>
</tr>
<tr>
<td>$c_B$</td>
<td>Bulk concentration of absorbent</td>
<td>mol/L</td>
<td>0.1 – 8$^\dagger$</td>
</tr>
<tr>
<td>$k_{L,CO_2}$</td>
<td>Liquid-phase mass-transfer coefficient</td>
<td>cm/s</td>
<td>$10^{-2}$</td>
</tr>
<tr>
<td>$c_{i,CO_2}$</td>
<td>Concentration of CO$_2$</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>

$^\dagger$depending on the corrosive nature, typically less than 1.0 mol/L
Rate of Absorption

- **Gas-phase:**

\[ J_{G,CO_2} = c_{CO_2} G \quad D_{G,CO_2} \frac{dc_{CO_2}}{dz} \bigg|_i = c_{CO_2} G \quad D_{G,CO_2} \left( c_{G,CO_2} \quad c_{i,CO_2} \right) \]

\[ = c_{CO_2} G \quad k_{G,CO_2} \left( c_{G,CO_2} \quad c_{i,CO_2} \right) \]

- **Liquid-phase:**

\[ J_{L,CO_2} = c_{CO_2} L \quad D_{L,CO_2} \frac{dc_{CO_2}}{dz} \bigg|_i = c_{CO_2} L \quad D_{L,CO_2} \left( c_{i,CO_2} \quad c_{L,CO_2} \right) \]

\[ = c_{CO_2} L \quad k_{L,CO_2} \left( c_{i,CO_2} \quad c_{L,CO_2} \right) \]

These equations may be used to then determine the number and height of the mass-transfer units to determine the design of the absorption (or stripping tower).
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:
    \[
    \text{Power} = \frac{dw_f}{dt} = \frac{\dot{m}\Delta p}{\rho \cdot \varepsilon}
    \]
  - Blowers handle $3 < \Delta P < 500$ kPa
  - For adiabatic and reversible compression of an ideal gas, blowing power is:
    \[
    \text{Power} = \frac{dw_b}{dt} = \frac{\dot{m}RT_1 k}{M(k - 1)\varepsilon} \left[ \left( \frac{p_2}{p_1} \right)^{(k-1)/k} - 1 \right]
    \]
    $T_1$ 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$_2$ to 10 MPa is recommended for pipeline transport.
- Adiabatic single-stage compression power can be calculated for an ideal gas by:

$$P_{ad} = \frac{\dot{m}RT}{M} \frac{k}{k-1} \left( r^{(k-1)/k} - 1 \right)$$

Such that $\dot{m}$ 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$_2$ from 1 atm (0.101 MPa) to 10 Mpa $\sim$ 20 kJ/mol CO$_2$.
- Rochelle et al. report significantly lower compression ($\sim$ 10 kJ/mol CO$_2$) 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$_2$. 
Real Work – Total

- Total real work required for CO$_2$ capture includes:
  - $W_{fan} + W_{pump} + W_{regen} + W_{comp}$

- On average, estimates for an amine-based absorption process (from IECD):
  - $W_{fan} \sim 7$ kJ/mol CO$_2$
  - $W_{pump} \sim 0.5$ kJ/mol CO$_2$
  - $W_{regen} \sim 39$ kJ/mol CO$_2$
  - $W_{comp} \sim 23$ kJ/mol CO$_2$ [1 atm → 10 MPa]
Capture processes

**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

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

1. Total Cost
   - Capital cost
     - MTZ and bed height
     - Sorption rate
       - Physisorption or Chemisorption (Equilibrium)
       - Diffusion (Time)
       - Sorption capacity
         - % Capture
       - 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)
- Common sorbents: activated carbon, zeolites, MOFs, etc.
Zeolite Properties

- Silicon and aluminum atom structures tetrahedrally bonded with oxygen
- Aluminum typically exists in a 3+ oxidation state, so will have a charge of -1 when tetrahedrally bonded
- Cations (positive charges) are used to stabilize these charges, distributing themselves in a way to minimize the free energy of the system

How do zeolites work to separate $N_2$ from $O_2$ or $CO_2$ from $N_2$?
- They actually prefer to adsorb $N_2$
- The interaction energy between ions and $N_2$ are much stronger than ions and $O_2$
  - $O_2$-Na+ (20 kJ/mol); $N_2$-Na+ (36 kJ/mol)
  - $O_2$-Li+ (32 kJ/mol); $N_2$-Li+ (51 kJ/mol)
- $N_2$ has a higher quadrupole moment than $O_2$
- Adsorption is dependent upon the interaction energy between 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
## Kinetic and Electrostatic Properties of Gases

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Kinetic Diameter (nm)</th>
<th>Dipole Moment (Debye)</th>
<th>Quadrupole Moment (10^{-40} Coulomb·m^2)</th>
<th>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>
</tr>
<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>
Zeolite Framework

SOD

LTA

FAU

sodalite
or β-cage
MOF Framework

(a) $\text{Zn}_4(\text{O})\text{O}_{12}\text{C}_6$ cluster + organic linker → 8 clusters comprise the 18.5 Å diameter

(b) And (c) show MOF structural features
## 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.

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

• 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?

\[ Power = P_1 V_1 \left( \frac{k}{k-1} \right) \left[ \left( \frac{P_2}{P_1} \right)^{(k-1)/k} - 1 \right] \]

- 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
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)
        - Stage cut
          - % Capture
        - Permeate mole fraction (purity)
          - 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.
Important Terms:
Stage cut = permeate flow rate/feed flow rate
Permeate/Residue Concentrations
Pressure Ratio = permeate pressure/feed pressure
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 \( \text{ft}^3/\text{ft}^2 \text{ h atm} \)
- 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
Robeson Plots

(a) CO₂/N₂
(b) H₂/CO₂
(c) CO₂/CH₄
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

Source: Richard Baker, Membrane Technology and Applications
Short-Cut Design Calculation

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

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

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

\( \frac{P_1}{l} \) is permeance of species 1

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

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

Selectivity and pressure ratio effects on the local permeate concentration
Capture processes

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

% Capture
% Purity

Thermodynamic minimum work

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

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

\[ \text{2nd law: } \frac{W_{\text{real}}}{W_{\text{min}}} = \]
Additional Slides
## 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>$k \left( \frac{1}{vg} \right)^{1/3} = 0.0051 \left( \frac{u}{va} \right)^{0.67} \left( \frac{D}{v} \right)^{0.5} (ad)^{0.4}$</td>
<td>Known as best available correlation for liquids</td>
</tr>
<tr>
<td></td>
<td>$\frac{kl}{D} = 25 \left( \frac{lu}{v} \right)^{0.45} \left( \frac{v}{D} \right)^{0.5}$</td>
<td>Classical result and widely referenced</td>
</tr>
<tr>
<td>Gas bubbles in stirred tank</td>
<td>$\frac{kl}{D} = 0.13 \left( \frac{(P/V)l^{4/3}}{\rho v^3} \right)^{1/4} \left( \frac{v}{D} \right)^{1/3}$</td>
<td>$k$ is not dependent on bubble size</td>
</tr>
<tr>
<td>Gas bubbles in unstirred tank</td>
<td>$\frac{kl}{D} = 0.31 \left( \frac{l^3 g \Delta \rho / \rho}{v^2} \right) \left( \frac{v}{D} \right)^{1/3}$</td>
<td>$\Delta \rho = $ density difference between bubble and fluid</td>
</tr>
<tr>
<td>Falling films</td>
<td>$\frac{kz}{D} = 0.69 \left( \frac{zu}{D} \right)^{0.5}$</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
## 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>Activated carbon</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>7</td>
<td>-</td>
</tr>
<tr>
<td>Zeolites</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>-</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>Silica gel</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>Activated alumina</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-7.5</td>
<td>800</td>
<td>0.50</td>
<td>320</td>
<td>7</td>
<td>2</td>
<td>150-315</td>
<td></td>
</tr>
<tr>
<td>MOFs</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>Ion exchange resins</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>Hollow fibers</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>CMS</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>Amine-based</td>
<td>8-40</td>
<td>1000-1500</td>
<td>5-500</td>
<td>-</td>
<td>5-14</td>
<td>-</td>
<td>80-120</td>
</tr>
<tr>
<td>Hydrotalcites</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>Chemisorbents</td>
<td>0.2-20</td>
<td>2000</td>
<td>250-1250</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>c700-920</td>
</tr>
</tbody>
</table>

a: 14a, 28
b: 12c, 33
c: 150-500
d: 350
Influence of Pressure Ratio

• Original Case:
  – 100 MSCFH natural gas
  – Feed pressure = 480 psia
  – Permeate pressure = 20 psia
  – $\Delta P = 460 \text{ psia}$
  – Pressure ratio, $\gamma = 0.042$
  – Feed CO$_2$ = 12%
  – Product CO$_2$ = 2%
  – Area required = 1,700 ft$^2$

• New Case:
  – 100 MSCFH natural gas
  – Feed pressure = 1200 psia
  – Permeate pressure = 200 psia
  – $\Delta P = 1000 \text{ psia}$
  – Pressure ratio, $\gamma = 0.17$
  – Feed CO$_2$ = 12%
  – Product CO$_2$ = 2%
  – Area required = 7,800 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.