Concept Design of a Double Effect Thermochemical Heat Pump Using the CaCl$_2$-NH$_3$ and the MgCl$_2$-NH$_3$ Pairs

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Introduction
The Rationale Behind Double Effect Thermochemical Heat Pumps

- Physical adsorbents such as activated carbon may take or desorb up to 20% of their own weight per cycle
- Salts perform much better. For instance, CaCl\(_2\) can take up refrigerant up to its own weight
- Single effect thermochemical heat pumps can attain COPs which are higher than those of physical adsorption heat pumps
- However, internal heat recovery within the system can help to further improve these COPs
Determination of Kinetic Parameters

• Heat of reaction can only be recovered at high power levels
• Reaction can only be partially completed
• Therefore, kinetics and heat transfer through the adsorbent bed must be studied. We must know how fast/slow these reactions happen!!!
Determination of Kinetic Parameters

**Relevant Reactions**

\[ \text{R1: } \text{CaCl}_2 \cdot 8\text{NH}_3 \rightarrow \text{CaCl}_2 \cdot 4\text{NH}_3 + 4\text{NH}_3 \]

\[ \text{R2: } \text{CaCl}_2 \cdot 4\text{NH}_3 \rightarrow \text{CaCl}_2 \cdot 2\text{NH}_3 + 2\text{NH}_3 \]

\[ \text{R1: } \text{MgCl}_2 \cdot 6\text{NH}_3 \rightarrow \text{MgCl}_2 \cdot 2\text{NH}_3 + 4\text{NH}_3 \]

**Relevant Equations**

\[ \ln(P) = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \]

<table>
<thead>
<tr>
<th></th>
<th>$\Delta H$ (Jmol$^{-1}$)</th>
<th>$\Delta S$ (Jmol$^{-1}$K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>R1</strong></td>
<td>41413</td>
<td>230.3</td>
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<tr>
<td><strong>R2</strong></td>
<td>42286</td>
<td>229.92</td>
</tr>
<tr>
<td><strong>Synthesis</strong></td>
<td>46677</td>
<td>118.53</td>
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<tr>
<td><strong>Decomposition</strong></td>
<td>60456</td>
<td>145.06</td>
</tr>
</tbody>
</table>

Determination of Kinetic Parameters

Sample Preparation and Details

<table>
<thead>
<tr>
<th>Thickness (mm)</th>
<th>Diameter (mm)</th>
<th>Mass of ENG (g)</th>
<th>Mass of CaCl₂ (g)</th>
<th>Density (kgm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>4.00</td>
<td>1.026</td>
<td>0.774</td>
<td>205</td>
</tr>
<tr>
<td>Sample 2</td>
<td>7.30</td>
<td>1.026</td>
<td>1.264</td>
<td>205</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Thickness (mm)</th>
<th>Diameter (mm)</th>
<th>Mass of ENG (g)</th>
<th>Mass of MgCl₂ (g)</th>
<th>Density (kgm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>4.00</td>
<td>0.775</td>
<td>0.585</td>
<td>173.25</td>
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</tbody>
</table>
Determination of Kinetic Parameters

*Large Temperature Jump Apparatus*

A. NH$_3$ reservoir  
B. Test Cell  
C. Circulating Baths  
D. Temperature control container
Determination of Kinetic Parameters

Large Temperature Jump Apparatus

The model used is a coupling between heat transfer and kinetics. It is made up of:

- A thermal part component
  \[ mC \frac{\partial T}{\partial t} = ks \frac{\partial T}{\partial z} - N_{NH_3} \Delta H \frac{\partial X}{\partial t} \]

- A kinetic component
  \[ \frac{\partial X}{\partial t} = (1 - X)^{\gamma} \ A \ P - P_{eq}\left( T \right) \]
Determination of Kinetic Parameters

Large Temperature Jump Apparatus

\[ \text{RMSE} = \sum_{i=1}^{tp} \sqrt{\frac{(P - P_d)^2}{tp}} \]

<table>
<thead>
<tr>
<th></th>
<th>A (s(^{-1}))</th>
<th>yo</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCl(_2)-NH(_3) (R1)</td>
<td>a 0.037</td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td>b 0.02</td>
<td>0.71</td>
</tr>
<tr>
<td>CaCl(_2)-NH(_3) (R2)</td>
<td>a 0.0069</td>
<td>0.81</td>
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<tr>
<td></td>
<td>b 0.0057</td>
<td>0.83</td>
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<tr>
<td>MgCl(_2)-NH(_3) (R1)</td>
<td>a 0.00013</td>
<td>0.64</td>
</tr>
<tr>
<td></td>
<td>b 0.000056</td>
<td>0.72</td>
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</table>
System Design and Concept

**Graphs and Diagrams:**

- **Graph A:**
  - abscissa: \( \ln P \) vs. \( T \)
  - annotations: \(-1/T\), \( \text{NH}_3 \), \( \text{CaCl}_2 \), \( \text{MgCl}_2 \)
- **Graph B:**
  - Similar to Graph A
- **Diagram C:**
  - Condenser connected to \( \text{MgCl}_2 \)
  - Evaporator connected to \( \text{CaCl}_2 \)
- **Diagram D:**
  - Condenser connected to \( \text{CaCl}_2 \)
  - Evaporator connected to \( \text{MgCl}_2 \)
Energy Equations

The Reactor ($\text{MgCl}_2$)

\[ Q_{\text{dec}(\text{MgCl}_2)} = \Delta H_{\text{sensible}} + \Delta H_{\text{reaction}} \]

\[ Q_{\text{dec}(\text{MgCl}_2)} = \int_{T_{\text{syn}(\text{MgCl}_2)}}^{T_{\text{dec}(\text{MgCl}_2)}} (m_{\text{MgCl}_2} + m_{\text{NH}_3(\text{MgCl}_2)}) C_{\text{p, MgCl}_2 + \text{NH}_3} dt + m_{\text{NH}_3(\text{MgCl}_2)} \Delta H_{\text{MgCl}_2(6-2)\text{NH}_3} \]

\[ Q_{\text{acc}(\text{MgCl}_2)} = (m_{\text{MgCl}_2} + m_{\text{NH}_3(\text{MgCl}_2)}) C_{\text{p, MgCl}_2 + \text{ENG} + \text{NH}_3} \left( T_{\text{dec}(\text{MgCl}_2)} - T_{\text{syn}(\text{MgCl}_2)} \right) + m_{\text{NH}_3(\text{MgCl}_2)} \Delta H_{\text{MgCl}_2(6-2)\text{NH}_3} \]
Energy Equations

Condenser

\[ \begin{align*}
4\text{NH}_3 \text{ gas} & \rightarrow \text{Condenser (gas)} \rightarrow 4\text{NH}_3 \text{ liquid} \\
\text{T}_{\text{dec}}(\text{MgCl}_2) & \rightarrow \text{NH}_3 \text{ gas at } T_{\text{dec}}(\text{MgCl}_2) \rightarrow \text{NH}_3 \text{ gas at } T_{\text{con}} \\
\Delta H_{\text{sensible}} & \rightarrow \text{NH}_3 \text{ gas} \rightarrow \Delta H_{\text{con}(\text{MgCl}_2)} \\
\text{NH}_3 \text{ liquid at } T_{\text{con}} & \rightarrow \text{NH}_3 \text{ liquid at } T_{\text{con}} \\
\end{align*} \]

\[ Q_{\text{con}(\text{MgCl}_2)} = \Delta H_{\text{sensible}} + \Delta H_{\text{con}(\text{MgCl}_2)} \]

\[ Q_{\text{con}(\text{MgCl}_2)} = \int_{T_{\text{dec}(\text{MgCl}_2)}}^{T_{\text{con}}} m_{\text{NH}_3(\text{MgCl}_2)} C_{p_{\text{NH}_3}} dT + m_{\text{NH}_3(\text{MgCl}_2)} \Delta H_{\text{con}(\text{MgCl}_2)} \]

\[ Q_{\text{con}(\text{MgCl}_2)} = m_{\text{NH}_3(\text{MgCl}_2)} \left( \Delta H_{\text{con}(\text{MgCl}_2)} + (C_{p_{\text{NH}_3}} (T_{\text{dec}(\text{MgCl}_2)} - T_{\text{con}}) \right) \]
Energy Equations

Evaporator

\[ Q_{ev(MgCl_2)} = \Delta H_{sensible} + \Delta H_{evaporation} \]

\[ Q_{ev(MgCl_2)} = \int_{T_{con}}^{T_{ev}} m_{NH_3(MgCl_2)} C_{pNH_3} dT + m_{NH_3(MgCl_2)} \Delta H_{evap(NH_3)} \]

\[ Q_{ev(MgCl_2)} = m_{NH_3(MgCl_2)} \left( \Delta H_{evap(MgCl_2)} + (C_{pNH_3}(T_{con} - T_{ev})) \right) \]
Energy Equations

Coefficient of Performance (COP) and Specific Heating Power (SHP)

- Higher COP expected from double effect system
- Specific heating power is in W/m³

\[ \text{COP}_{\text{CaCl}_2} = \frac{Q_{\text{con(CaCl}_2)} + Q_{\text{syn(CaCl}_2)}}{Q_{\text{dec(CaCl}_2)}} \]

\[ \text{COP}_{\text{MgCl}_2} = \frac{Q_{\text{con(MgCl}_2)} + Q_{\text{syn(MgCl}_2)}}{Q_{\text{dec(MgCl}_2)}} \]

\[ \text{COP}_{\text{CaCl}_2 & \text{MgCl}_2} = \frac{Q_{\text{con(MgCl}_2)} + Q_{\text{con(CaCl}_2)} + Q_{\text{syn(CaCl}_2)}}{Q_{\text{dec(MgCl}_2)}} \]

\[ \text{SHP}_{\text{CaCl}_2} = \frac{Q_{\text{con(CaCl}_2)} + Q_{\text{syn(CaCl}_2)}}{V_{\text{CaCl}_2}} \]

\[ \text{SHP}_{\text{MgCl}_2} = \frac{Q_{\text{con(MgCl}_2)} + Q_{\text{syn(MgCl}_2)}}{V_{\text{MgCl}_2}} \]

\[ \text{SHP}_{\text{CaCl}_2 & \text{MgCl}_2} = \frac{Q_{\text{con(CaCl}_2)} + Q_{\text{con(MgCl}_2)} + Q_{\text{syn(CaCl}_2)}}{V_{\text{CaCl}_2 & \text{MgCl}_2}} \]
Performance Analysis (Ongoing)

- Early COP results show an increase of 26% in COP compared to single effect

**Important Results**

- Effects of external heat source temperature
- Effects of CaCl$_2$-MgCl$_2$ mass ratio
- Effects of internal heat recovery time
- Effects of overall cycle time
- Effects of metal thermal mass
Thank you!!!
Any Questions??