Modelling and Large Temperature Jump Testing of the $\text{CaCl}_2$-$\text{NH}_3$ Reaction

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Introduction

- 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.
- However, they swell and agglomerate when reacting. This is addressed by infusing them in host matrices (expanded graphite) to allow for the swelling.
Introduction

\[ \text{Salt} + n\text{NH}_3 \rightleftharpoons n\text{NH}_3 \cdot \text{Salt} + n\Delta H_{\text{reaction}} \]

• 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 these reactions happen.
Introduction

• Two relevant reactions

\[ \text{R1: CaCl}_2.8\text{NH}_3 \rightleftharpoons \text{CaCl}_2.4\text{NH}_3 + 4\text{NH}_3 \]
\[ \text{R2: CaCl}_2.4\text{NH}_3 \rightleftharpoons \text{CaCl}_2.2\text{NH}_3 + 2\text{NH}_3 \]

• Governed by the Clausius-Clapeyron relationship:

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

<table>
<thead>
<tr>
<th></th>
<th>( \Delta H ) (Jmol(^{-1}))</th>
<th>( \Delta S ) (Jmol(^{-1})K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>41413</td>
<td>230.30</td>
</tr>
<tr>
<td>R2</td>
<td>42286</td>
<td>229.92</td>
</tr>
</tbody>
</table>

Sample Preparation and Details

**Table 2: Details of experiments**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness (mm)</th>
<th>Diameter (mm)</th>
<th>Mass of ENG (g)</th>
<th>Mass of CaCl₂ (g)</th>
<th>Temperature Range (°C)</th>
<th>Starting Pressure (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>4.0</td>
<td>50</td>
<td>1.026</td>
<td>0.774</td>
<td>50-90</td>
<td>5.75</td>
</tr>
<tr>
<td>Sample 2</td>
<td>7.2</td>
<td>50</td>
<td>1.026</td>
<td>1.264</td>
<td>50-90</td>
<td>5.75</td>
</tr>
</tbody>
</table>

Density of 205kg/m³
Experimental Apparatus and Procedure
(Large Temperature Jump)

A. NH₃ reservoir
B. Test Cell
C. Circulating Baths
D. Temperature control container
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**
  
  \[
  \frac{\partial X}{\partial t} = (1 - X)^y A \frac{P - P_{eq}(T)}{P}
  \]
Solution of the Model

The model is solved by treating the sample as a discretised volume split into layers.

\[
\Delta m C \left( \frac{T_i^j - T_{i-1}^j}{\Delta t} \right) = k_s \left( \frac{T_{i-1}^{j-1} - T_{i-1}^j}{\Delta z} \right) + k_s \left( \frac{T_{i-1}^{j+1} - T_{i-1}^j}{\Delta z} \right) - N_{NH_3} \Delta H \frac{\Delta X_i^j}{\Delta t}
\]

\[
\frac{\Delta X_i^j}{\Delta t} = (1 - X_{i-1}^j)^y A \frac{P_{di} - P_{eqi-1}^j}{P_{di}}
\]

\[
\frac{\partial T}{\partial z \text{ top boundary}} = 0
\]

\[
T(t = 0)_{\text{all discrete volumes}} = T_1^j
\]
Results (Kinetic Parameter (A))

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

<table>
<thead>
<tr>
<th>A</th>
<th>0.01</th>
<th>0.02</th>
<th>0.03</th>
<th>0.04</th>
<th>0.05</th>
<th>0.06</th>
<th>0.07</th>
</tr>
</thead>
<tbody>
<tr>
<td>RMSE</td>
<td>0.050195</td>
<td>0.022681</td>
<td>0.010172</td>
<td>0.004068</td>
<td>0.004595</td>
<td>0.007245</td>
<td>0.009448</td>
</tr>
</tbody>
</table>

R1: \( \text{CaCl}_2 \cdot 8\text{NH}_3 \rightleftharpoons \text{CaCl}_2 \cdot 4\text{NH}_3 + 4\text{NH}_3 \)

R2: \( \text{CaCl}_2 \cdot 4\text{NH}_3 \rightleftharpoons \text{CaCl}_2 \cdot 2\text{NH}_3 + 2\text{NH}_3 \)

<table>
<thead>
<tr>
<th></th>
<th>R1</th>
<th>R2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decomposition</td>
<td>0.04</td>
<td>0.05</td>
</tr>
<tr>
<td>Synthesis</td>
<td>0.06</td>
<td>0.04</td>
</tr>
</tbody>
</table>
Example Temperature Profile Results (R1, 58-76°C & 76-58°C)
Example Temperature Profile
Results (R2, 76-87°C & 87-76°C)
Example Advancement Profile

Results (R1, 58-76°C & 76-58°C)
Example Advancement Profile Results (R2, 76-87°C & 87-76°C)
Comparison Between Sample 1 (4mm) and Sample 2 (7.3mm) (R1, 58-76°C)

(4mm) vs (7.2mm)
Results (Sensitivity to Thermal Conductivity)
Going Ahead....

- Repeat the same process for a higher temperature salt (MgCl$_2$)
- Use the results obtained in the design of a double effect cascaded CaCl$_2$-MgCl$_2$ thermochemical heat pump
Thank you!!!