Modelling of liquid-vapor-solid equilibria in the NH$_3$-CO$_2$-H$_2$O system

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Introduction

• CO₂ capture by amines is state-of-the-art technology

• Characteristics of a desired technology
  – Temperature stability over a temperature range
  – High selectivity for CO₂
  – Non-corrosive
  – High cycle life
  – Low energy regeneration (stripping)
  – Rapid kinetics for scrubbing and stripping

• Can ammonia processes challenge amines with respect to
  – energy requirements
  – reduced environmental impact
Ammonia for CO$_2$ capture

• Used in De-NOx processes & to remove SO$_2$ and HCl

• Low environmental impact

• Several approaches on the thermodynamics

• Tool to predict phase behavior, mass & energy balances
Components & equilibrium reactions

<table>
<thead>
<tr>
<th>Vapour</th>
<th>Aqueous</th>
<th>Solids</th>
<th>CH$_4$, N$_2$, O$_2$, Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>CO$_2$ + H$_2$O ↔ H$^+$ + HCO$_3^-$</td>
<td>NH$_4^+$ + HCO$_3^-$ ↔ NH$_4$HCO$_3$(s)</td>
<td></td>
</tr>
<tr>
<td>NH$_3$</td>
<td>HCO$_3^-$ ↔ H$^+$ + CO$_3^{2-}$</td>
<td>NH$_3$ + HCO$_3^-$ ↔ NH$_2$COO$^-$ + H$_2$O</td>
<td></td>
</tr>
<tr>
<td>H$_2$O</td>
<td>NH$_4^+$ ↔ H$^+$ + NH$_3$</td>
<td>H$_2$O ↔ H$^+$ + OH$^-$</td>
<td></td>
</tr>
</tbody>
</table>

Soave- Redlich- Kwong EOS for gas fugacities

Henry’s law

Pitzer model & equilibrium constants

Solubility product

Pure solids

Solubility product
Thermal model

- Heat capacities, standard state enthalpies & entropies were used

\[ \cdot H_f^T = \cdot H_f^0 + \int_0^T C_{p(i)}(T) \, dt \]

- For water:  
  \[ c_{p(H_2O)} = c_{p,A} + c_{p,B} \cdot T + \frac{c_{p,C} \cdot 10^{-5}}{T^2} + c_{p,D} \cdot 10^{-6} T^2 \]

- Aqueous & dissolved species:  
  \[ c_{p(i)} = c_{p,A} + c_{p,B} \cdot T + \frac{c_{p,C}}{T - 200} \]

- Solid(s): treated as particles/species in a water stream

- Gas components:
  \[ c_{p(i)} = c_{pA} + c_{pB} \cdot T + c_{pC} \cdot T^2 + c_{pD} \cdot T^3 \]

  residual term: calculated through the EOS
Data

- Model is based entirely on open literature data
- Approximately 3500 experimental data on:
  - VLE
  - SLE
    - heat capacities, enthalpies, entropies
- Scattered SLE data
- NH$_4$HCO$_3$(s) of primary importance
- Other possible salts: (NH$_4$)$_2$CO$_3$
  - NH$_4$CO$_2$NH$_4$
  - NH$_4$HCO$_3$- NH$_4$CO$_2$NH$_2$
  - (NH$_4$)$_2$CO$_3$- NH$_4$HCO$_3$- H$_2$O
Model testing – \( \text{NH}_3\)-\( \text{CO}_2\)-\( \text{H}_2\text{O} \) system

Data from:
- Pexton and Badger (1938)
- Van Krevelen et al. (1949)
- Otsuka et al. (1960)
- Kurz et al. (1995)
- Verbrugge (1979)
- Göppert and Maurer (1988)
- Müller et al. (1988)
- Pawlikowski et al. (1982)
- Mezger and Payer (1925)

\( \text{NH}_3 \): 0.5-13 mole/kg \( \text{H}_2\text{O} \)

\( \text{CO}_2 \): up to 15 mole/kg \( \text{H}_2\text{O} \)

Reliable results at least up to 100°C
Model testing – NH$_4$HCO$_3$ solubility

Data from: Jänecke (1927), Jänecke (1929)

Supersaturation, SR

\[
SR = \frac{[\text{NH}_4^+][\text{HCO}_3^-]}{K_{sp}(\text{NH}_4\text{HCO}_3)}
\]

SR=1 perfect match
SR>1 model predicts too low solubility
SR<1 model predicts too high solubility

Data from: Jänecke (1927), Jänecke (1929)
Simulation tool

- Excel based process simulator, thermodynamic calculations in dll
Application in a generic ammonia process

- Powerspan’s ECO$_2$® technology
- CSIRO’s ammonia PCC
- CAER pilot studies (Univ. of Kentucky)
Simulation results

**NH₃ in cleaned gas**

3.5% CO₂, G: 10 kg/s, L: 200 kg/s, (NH₄)₂CO₃: 3,4,6 mol/L

**Cooling duty of flue gas**

3.5% CO₂, G: 10 kg/s, L: 200 kg/s, (NH₄)₂CO₃: 4 mol/L
Simulation results

Energy needed to heat CO₂ rich stream

T(regen): 60, 70, 80, 90°C, T(abs): 12, 20, 35°C
Thank you

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Backup slides
Calculations

- Calculate thermodynamic equilibrium and other P-T constants
- EOS solved for gas $\rightarrow$ fugacity coefficients
- Pitzer solved for aqueous components $\rightarrow$ activity coefficients
- Equilibria, mass balances for CO2, NH3, H2O & alkalinity equation
- Update EOS and SRK with new values

- Typically 3-6 iterations
Parameters & simplifications in Pitzer model

• Similar to Bieling et al. (1995)

• Theoretically: 36 binary and 120 ternary parameters

• Interactions neglected:
  − $\frac{H^+}{[OH^-]} << \text{NH}_3/\text{NH}_4^+$ and $\text{CO}_2/\text{HCO}_3^-/\text{CO}_3^{2-}$
  − $\text{CO}_2$ and $\text{NH}_3$ cannot coexist
  − ions of the same sign
  − ion and a neutral

• Ternary parameters: important only at very high concentrations

• Same approach for triple interactions
NH₃ solubility – Comparison with HYSYS

- Different fluid packages in HYSYS - non ideal behaviour of NH₃ in water
- Solubility of NH₃ is calculated and compared to various models