Thermodynamic behaviour of mixtures containing CO$_2$. A molecular simulation study

V. Lachet, C. Nieto-Draghi, B. Creton (IFPEN)

Å. Ervik, G. Skaugen, Ø. Wilhelmsen, M. Hammer (SINTEF)
Impure CO₂ may have significantly different thermo-physical properties compared to pure CO₂.

Needs for accurate knowledge of the thermodynamic and transport properties of CO₂ + associated gas mixtures in order to develop optimized transport solutions.
Outline

- Simulation methods
  - Monte Carlo and Molecular Dynamics
  - Application to the calculation of pure CO$_2$ properties
- Thermodynamic study of CO$_2$ + N$_2$O mixtures
  - Intermolecular potential for nitrous oxide
  - Vapor-liquid phase diagrams
  - Densities and viscosities
- Thermodynamic study of CO$_2$ + NO mixtures
  - Intermolecular potential for nitric oxide
  - Vapor-liquid phase diagrams
  - Densities and viscosities
- Thermal conductivity of mixtures
  - Intermolecular potentials for O$_2$, N$_2$, and H$_2$S
  - Application to CO$_2$ + N$_2$, CO$_2$ + O$_2$, and CO$_2$ + H$_2$S
Simulation methods

Molecular simulation methodologies

Two ways of generating a statistical ensemble

Monte Carlo: Statistical method (Markov chain + Metropolis algorithm) ensuring occurrence of configuration $i \sim \exp(-U_i/kT)$

Molecular Dynamics:

Integration of Newton’s equations of motion

$\Delta t = 1 \text{ to } 2 \text{ fs}$

$m\Delta t = 4 \text{ to } 5 \text{ ns}$

$\langle X \rangle_{MD} = \frac{1}{t} \int_{t_1}^{t} X(t) dt$

Representative array of $n$ configurations ($n > 5.0 \times 10^7$)

$\langle X \rangle_{MC} = \frac{1}{n} \sum_{i=1}^{n} (X_i)$

averages for property $X = V, U, ...$

Ergodicity theorem: $\langle X \rangle_{MD} = \langle X \rangle_{MC}$
Simulation methods

Molecular simulation methodologies
Non-Equilibrium Molecular Dynamics

Select particle with lowest kinetic energy
Select particle with highest kinetic energy

\[
\begin{align*}
\text{old } h &= v \\
\text{new } h &= v + \\
\text{old c} &= v \\
\text{new c} &= v \\
\end{align*}
\]

\[
\begin{align*}
T (K) & 0 & 20 & 40 & 60 & 80 & 100 \\
J_q (W/m^2) & 0 & 0.03 & 0.04 & 0.05 & 0.06 \\
z (\text{Å}) & 250 & 300 & 350 & 400 \\
t (\text{ps}) & 0 & 1000 & 2000 & 3000 & 4000 \\
\end{align*}
\]
Simulation methods

Intermolecular potential used for CO$_2$

Harris and Yung (1995)

- Rigid molecule
- Three 6-12 Lennard-Jones centers + three point charges

Lennard-Jones potential

$$U_{disp-rep}^{ij} = 4\varepsilon \left( \frac{\sigma_{ij}^{12}}{r_{ij}^{12}} - \frac{\sigma_{ij}^6}{r_{ij}^6} \right)$$

Electrostatic energy

$$U_{el}^{ij} = \frac{q_i q_j}{4\pi\varepsilon_o r_{ij}}$$

Simulation methods

Pure CO$_2$ properties
Thermodynamic and transport properties

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Simulation results
Experimental data

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Simulation results
Experimental data

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Simulation results
Experimental data

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Simulation results / Liq.
Simulation results / Vap.
Experimental data
Two sets of parameters are available in the literature:

- Costa Gomes et al. (2006)
- Hansen et al. (2007)

- Rigid molecule (geometry taken from Chase, 1985)
- Three 6-12 Lennard-Jones centers + three point charges

CO₂-N₂O mixtures

Intermolecular potential for N₂O
Optimization of force field parameters

• Minimization of the error function (Ungerer et al., JCP, 112, 5499, 2000):

\[
F = \frac{1}{n} \sum_{i=1}^{n} \left( \frac{f_i^{\text{calc}} - f_i^{\text{exp}}}{s_i} \right)^2
\]

where \( s_i \) = statistical uncertainty on \( f_i = \rho, \Delta H_{\text{vap}}, \ln(P_{\text{sat}}) \)

• Searching for the minimum using the gradient method

• Calculation of partial derivatives of \( F \) from statistical fluctuations (NVT ensemble):

\[
\frac{\partial \langle f_i^{\text{calc}} \rangle}{\partial \sigma_j} = \langle \frac{\partial f_i^{\text{calc}}}{\partial \sigma_j} \rangle - \beta \left( \langle f_i^{\text{calc}} \frac{\partial U}{\partial \sigma_j} \rangle - \langle f_i^{\text{calc}} \rangle \langle \frac{\partial U}{\partial \sigma_j} \rangle \right)
\]

Bourasseau et al., JCP, 118, 3020 (2003)

• Use of two temperatures in the error criterion (190 K and 270 K)

• Results:

\[\begin{align*}
\sigma_{N1} &= 3.116 \text{ Å}; \quad \varepsilon_{N1} = 78.107 \text{ K}; \quad q_{N1} = -0.34 \text{ e} \\
\sigma_{N2} &= 2.927 \text{ Å}; \quad \varepsilon_{N2} = 34.647 \text{ K}; \quad q_{N2} = +0.68 \text{ e} \\
\sigma_{O} &= 3.044 \text{ Å}; \quad \varepsilon_{O} = 65.891 \text{ K}; \quad q_{O} = -0.34 \text{ e}
\end{align*}\]
CO₂-N₂O mixtures

**Intermolecular potential for N₂O**

Accuracy of different force-fields

- Liquid-vapor coexisting densities

![Graph showing liquid-vapor coexisting densities for CO₂-N₂O mixtures with comparison to experimental data and different force fields.

Exp data: DIPPR data bank and Quinn (1929)

<table>
<thead>
<tr>
<th>Force Field</th>
<th>AAD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Costa Gomes</td>
<td>2.6%</td>
</tr>
<tr>
<td>Hansen</td>
<td>0.9%</td>
</tr>
<tr>
<td>New force field</td>
<td>1.0%</td>
</tr>
</tbody>
</table>

+ Good estimate of the critical coordinates
**CO₂-N₂O mixtures**

**Intermolecular potential for N₂O**

**Accuracy of different force-fields**

- **Vapor pressures**

![Graph showing vapor pressures for CO₂-N₂O mixtures with data points for different force-fields and experimental data.](image)

- **Costa Gomes**
  - AAD: 24.7%

- **Hansen**
  - AAD: 6.7%

- **New force field**
  - AAD: 5.8%

Exp data: DIPPR data bank
CO$_2$-N$_2$O mixtures

Intermolecular potential for N$_2$O

Accuracy of different force-fields

- Vaporization enthalpies

![Graph showing vaporization enthalpies for CO$_2$-N$_2$O mixtures with data points for different force-fields and experimental data from DIPPR data bank.](image)

Exp data: DIPPR data bank

- New force field: 3.5%
- Costa Gomes: 9.5%
- Hansen: 7.4%
CO\textsubscript{2}-N\textsubscript{2}O mixtures

Intermolecular potential for N\textsubscript{2}O

Accuracy of different force-fields

Exp data: NIST website

Costa Gomes 22.3 %
Hansen 35.2 %
New force field 11.8 %
**Study of CO₂-N₂O mixtures**

**Vapor-liquid phase diagrams**

- Good agreement between experimental and simulated data at 283 K and 293 K
- Strong similarities between CO₂ and N₂O (in terms of molecular weights, vapor pressures, critical coordinates...) => quasi-azeotropic system over the full range of compositions

Exp data:
Study of CO$_2$-N$_2$O mixtures
Densities and viscosities

- Pressure-density and pressure-viscosity diagram at 283 K and 293 K of a CO$_2$-N$_2$O mixture with 10 mol% of N$_2$O.

⇒ Excellent agreement between experimental and simulated data for pure CO$_2$
⇒ No significant impact of N$_2$O on both densities and viscosities

Exp data for CO$_2$: NIST website
**CO₂-NO mixtures**

**Study of NO**

Equilibrium between monomers and dimers

Nitric oxide: \(2 \text{NO} \leftrightarrow \text{N}_2\text{O}_2\)

Monte Carlo in the Reactive Ensemble

- **Constraints**
  - Fixed \(T\) and \(V\), or fixed \(T\) and \(P\)
  - Mass conservation
  - Equilibrium condition

- **Monte Carlo moves**
  - Usual moves performed in the NVT or NPT ensembles
  - Reaction move

\[
\sum_{i=1}^{s} v_i \mu_i = 0
\]

example: \(\mu(\text{N}_2\text{O}_2) = 2\mu(\text{NO})\)


**FIG. 2.** Mole fraction of \((\text{NO})_2\) dimers as a function of temperature \(T\) along the saturation line for the bulk liquid-phase \(2\text{NO} \leftrightarrow (\text{NO})_2\) system from the RxMC simulations and from the experiments. The lines are drawn as a guide to the eye.
Rigid molecules
No account of the polarity of the molecule ($\mu = 0.159$ D for NO)
NO: a unique 6-12 Lennard-Jones center
$\text{N}_2\text{O}_2$: two NO 6-12 Lennard-Jones centers separated by 2.237 Å

Several sets of parameters are available in the literature:

<table>
<thead>
<tr>
<th></th>
<th>$\sigma$ (Å)</th>
<th>$\varepsilon/k$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kohler et al. (1987)</td>
<td>3.171</td>
<td>125.0</td>
</tr>
<tr>
<td>Hirshfelder (1954)</td>
<td>3.599</td>
<td>91.0</td>
</tr>
<tr>
<td>Hirshfelder (1954)</td>
<td>3.470</td>
<td>119.0</td>
</tr>
<tr>
<td>+ one IFPEN force field</td>
<td>3.400</td>
<td>130.0</td>
</tr>
</tbody>
</table>

1 Lennard-Jones center

2 Lennard-Jones center

2.237 Å
CO₂-NO mixtures

Simulation of the NO + N₂O₂ system

Liquid-vapor equilibrium properties

Simultaneous use of the ReMC and GEMC methods

Temperature (K)

N₂O mole fraction

New force field
Kohler force field
Hirschfelder 1 force field
Hirschfelder 2 force field
Exp. data / Smith, 1952

Temperature (K)

N₂O₂ mole fraction
CO₂-NO mixtures

Simulation of the NO + N₂O₂ system

LVE properties: use of the ReMC and GEMC methods

![Graph showing temperature vs. density with data points for different force fields and experimental data.]

![Graph showing reciprocal temperature vs. saturation pressure with data points for different force fields and experimental data.]

![Graph showing temperature vs. vaporization enthalpy with data points for different force fields and experimental data.]
CO₂-NO mixtures

Study of CO₂-NO mixtures

Pressure-composition and pressure-density diagrams
Pressure-density and pressure-viscosity diagram at 263 K and 273 K of a CO₂-NO mixture with 10 mol% of NO.

⇒ Excellent agreement between experimental and simulated data for pure CO₂
⇒ Significant impact of NO on both liquid densities and viscosities

Exp data for CO₂: NIST website
Thermal conductivities

Intermolecular potentials for O₂, N₂, and H₂S

- **Rigid molecules**

  **O₂**
  
  2 Lennard-Jones centers
  \( \sigma_\text{O} = 3.11 \text{ Å} \) and \( \epsilon_\text{O} = 43.2 \text{ K} \)

  ![O₂ diagram](image)

  \( q = -2.1 \text{ e} \)
  \( q = 4.2 \text{ e} \)

  **N₂**
  
  2 Lennard-Jones centers
  \( \sigma_\text{N} = 3.33 \text{ Å} \) and \( \epsilon_\text{N} = 36.0 \text{ K} \)

  ![N₂ diagram](image)

  \( q = -0.5075 \text{ e} \)
  \( q = -0.5075 \text{ e} \)

  **H₂S**
  
  1 Lennard-Jones center
  \( \sigma_\text{S} = 3.73 \text{ Å} \) and \( \epsilon_\text{S} = 250.0 \text{ K} \)

  ![H₂S diagram](image)

  \( q = 1.015 \text{ e} \)
  \( q = -0.9 \text{ e} \)

Thermal conductivities

Study of CO_{2} + N_{2} systems

130 bar, 288K

150 bar, 288K

130 bar, 293K

150 bar, 293K
Thermal conductivities

Study of CO$_2$ + O$_2$ systems

130 bar, 288K

130 bar, 293K
Thermal conductivities

Study of CO$_2$ + H$_2$S systems

130 bar, 288K

130 bar, 293K
Development of new force fields and prediction of some property values for CO$_2$ + N$_2$O and CO$_2$ + NO mixtures.

- All results have been published:


Calculation of thermal conductivities for binary mixtures such as CO$_2$ + N$_2$, CO$_2$ + O$_2$ and CO$_2$ + H$_2$S.

- A publication is currently in preparation in collaboration with SINTEF.