Thermophysical Properties of Carbon Dioxide and CO$_2$-Rich Mixtures

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DOE UTSR Workshop, Purdue, Oct. 22, 2014
Motivation

1. Thermophysical properties of CO\(_2\) for design and optimization of sCO2 power cycles

2. For Carbon Capture and Sequestration (CCS), need to know phase behavior of water in compressed CO\(_2\) (condensation in pipelines, etc. leads to corrosion)
Outline

1. CO₂ Thermodynamic Properties (review)
2. CO₂ Thermal Conductivity: Measurements and Correlation
3. CO₂ Viscosity Correlation
4. Dew Point of Water in Compressed CO₂
5. Future Possibilities
Thermodynamic Properties of Pure CO₂

• Compute using Equation of State (EOS) $p(\rho,T)$
  [state-of-the-art: Helmholtz energy as $f(\rho,T)$]

• NOTE: EOS also needed for transport correlations [to
  get $\rho(p,T)$ and for critical enhancement]

• Old engineering EOS (Peng-Robinson, etc.) not accurate
  enough, especially around critical point.

• For well-measured fluid, can fit substance-specific
  reference EOS.

• Early standard EOS: Ely et al. (NBS), 1987.

Span-Wagner EOS for CO$_2$

- Up to 1100 K (1520 °F) and 800 MPa (116,000 psia)
- Extrapolation believed to be good beyond those limits
- Uncertainty similar to that of best data, should be negligible for engineering purposes
- Implemented in NIST REFPROP (and other software)
- Should be the benchmark for work with pure CO$_2$
- If too slow for an application (CFD), can pre-generate grids for spline interpolation
Thermal Conductivity of Pure CO$_2$

- Current correlation from 1990, based on older data and used older (1987) EOS.
- Uncertainties around 5% at many conditions (1% or 2% in some well-measured regions). Uncertainty due to limitations of existing data, especially at high T and/or P and near the critical point.

- Our plan:
  1. Take new data with lower uncertainty over wide range of conditions (Done)
  2. New correlation, using new data, Span-Wagner EOS, and theoretical guidance (in progress)
Thermal Conductivity Measurements

- Carbon dioxide sample purity of 99.994 %
- Subcritical thermal conductivity measured for liquid and vapor along 220, 237, 252, 267, 282, and 296 K isotherms
- Supercritical thermal conductivity measured along 310, 314, 324, 340, 370, 404, 453, 503, 553, 603, 652, 702, and 752 K isotherms
- Transient hot-wire measurements for liquid phase and for gas phase at pressures from 0.5 MPa to saturation or 69 MPa
- Steady-state hot-wire measurements for gas phase at pressures below 1 MPa
- Uncertainty is 0.5 % for liquid and compressed gas, increasing to 3 % for gas below 1 MPa and in the critical region
Schematic of Hot-Wire Bridge

- Main Power Relay
- Dummy Load Resistance
- Power Supply
- Hot-Wire Bridge
- Imbalance Voltage
- R1, R2, R3, R4
- +V/2, −V/2
- Ground
- Long Hot Wire
- Short Hot Wire
- Cell Wall
Working Equation (transient hot wire)

\[ \Delta T_{id} = \frac{q}{4\pi\lambda} \left[ \ln(t) + \ln\left(\frac{4a}{r_0^2 C}\right) \right] = \Delta T_w + \sum_{i=1}^{10} \delta T_i \]

\[ \Delta T_{id} \quad = \quad \text{ideal temperature rise (line heat source)} \quad (K) \]
\[ q \quad = \quad \text{applied power per unit length of wire} \quad (W/m) \]
\[ \lambda \quad = \quad \text{thermal conductivity} \quad (W/(m\cdot K)) \]
\[ t \quad = \quad \text{elapsed time} \quad (s) \]
\[ a \quad = \quad \text{thermal diffusivity} \quad (m^2/s) \]
\[ r_0 \quad = \quad \text{wire radius} \quad (m) \]
\[ C \quad = \quad \text{exponential of Euler’s Constant} \quad (1.781…) \]
\[ \Delta T_w \quad = \quad \text{measured temperature rise} \quad (K) \]
\[ \delta T_i \quad = \quad \text{corrections for non-ideal heat transfer} \quad (K) \]
Working Equation (Steady-State Hot Wire)

\[ \lambda = \frac{q}{2\pi(T_1 - T_2)} \left[ \ln \left( \frac{r_2}{r_1} \right) \right] \]

\( \lambda \) = thermal conductivity (W/(m·K))

\( q \) = applied power per unit length of wire (W/m)

\( r_1 \) = wire radius (m)

\( r_2 \) = concentric cavity radius (m)

\( T_1 \) = measured wire temperature (K)

\( T_2 \) = cell temperature (K)
Thermal Conductivity (Subcritical Vapor)

\[
\frac{\lambda}{\text{W.m}^{-1}\text{K}^{-1}} = \frac{\rho}{\text{kg.m}^{-3}}
\]

- 220 K
- 237 K
- 252 K
- 267 K
- 282 K
- 296 K

REFPROP
Thermal Conductivity: Liquid & Supercritical Phases

Graph showing the relationship between thermal conductivity ($\lambda$) in W m$^{-1}$ K$^{-1}$ and density ($\rho$) in kg m$^{-3}$ for different temperatures (314 K, 404 K, 503 K, 603 K, 702 K). The graph includes a line labeled "REFPROP" and another labeled "Critical Density."
Thermal Conductivity Critical Enhancement

- Saturation
- 1% Enhancement
- 5% Enhancement
- 10% Enhancement
- 25% Enhancement

$P/P_c$ vs $T/T_c$ graph

Critical Point
Thermal Conductivity Correlation

- Thermal conductivity expressed as sum of 3 contributions

\[ \lambda(\rho, T) = \lambda_0(T) + \lambda_1(\rho, T) + \lambda_2(\rho, T) \]

- Zero-Density contribution
- Critical enhancement
- Residual contribution
Zero-Density Limit

• Experimental data at density < 50 kg/m³ considered for regression
• Data sorted into “bins” of ~ 3 K; thermal conductivity corrected to nominal temperature

\[ \lambda_{\text{corr}}(T_{\text{nom}}, \rho) = \lambda_{\text{exp}}(T_{\text{exp}}, \rho) + [\lambda(T_{\text{nom}}, \rho) - \lambda(T_{\text{exp}}, \rho)]_{\text{calc}} \]

• Weighted linear least squares regression used to extrapolate to zero density resulting in set of experimental \( \lambda_0(T_r) \)
  o Results: 47 isotherms from 219 K to 751 K
• Experimental data supplemented by selected theoretical results from the work of Hellmann (2014)
  o Uncertainty of 1 % for 300 K < \( T < 700 \) K, increasing to 2 % at 150 K and 2000 K.
  o Added 8 points between 150 K and 215 K, 14 points between 760 K and 2000 K
Zero-Density Limit, continued

- Zero-density values fit to functional form:

\[
\lambda_0(T_r) = \frac{\sqrt{T_r}}{\sum_{k=0}^{J} \frac{L_k}{T_r^k}}
\]

\[T_r = T/T_c\]
Residual Contribution

- Identify primary data set and assess their uncertainties
- Fit primary experimental data \textit{simultaneously} for residual and critical enhancement terms.
- Use equation of state of Span and Wagner to provide density and thermodynamic properties required in enhancement term
- Theoretical guidance \textit{not} available for the residual contribution
- Use empirical form

\[
\lambda_1(T_r, \rho_r) = \sum_{j=1}^{m} (B_{1,j} + B_{2,j}T_r) \rho_r^j
\]
Selected (preliminary) Results

Supercritical Fluid, $T > 500$ K

![Graph showing data points for supercritical fluid at temperatures above 500 K. The graph includes data from various sources: Bakulin 1976, LeNeindre 1972, LeNeindre 1973, Perkins HTSS, Perkins HTTR, and Tarzimanov 1978.](image-url)
Selected (preliminary) Results

Significant improvements in representation of liquid phase
Our new data represented to \( \sim 1\% \)
Viscosity of Pure CO$_2$

- Uncertainties 4-5 % at many conditions (1 % or 2 % in some well-measured regions)
- Since 1998, some new data available, and better theoretical understanding (esp. for dilute gas)
- Our plan: New correlation, using new data, Span-Wagner EOS, and theoretical guidance
$p,T$-Distribution of Selected Viscosity Data
Viscosity Formulation

\[ \eta(T, \rho) = \eta_0(T) + \Delta \eta(T, \rho) + \Delta \eta_c(T, \rho) \]

Correlation for \( \rho \to 0 \) by Bock et al. (2002)

\[ \eta_0(T) = 0.021357 \sqrt{MT} / \sigma^2 \exp \left[ \sum_{i=0}^{4} a_i (\ln T^*)^i \right] \]

with \( T^* = T / (\varepsilon / k_B) \)

Residual part, Symbolic regression (preliminary)

\[ \Delta \eta(T, \rho) = \eta_{tL} \left[ a_1 \rho_r + a_2 \rho_r^{a_3} + (a_4 \rho_r)^{a_5} / T_r \right] \]

\[ \eta_{tL} = \frac{\rho_{tL}^{2/3} \sqrt{R T_t}}{M^{1/6} N_A^{1/3}} \]
Viscosity Data and Correlation for $\rho \to 0$
Data Representation by Preliminary Correlation
For carbon capture and sequestration (CCS), compressed CO$_2$ in pipelines will contain some H$_2$O.

Condensation of H$_2$O undesirable (corrosion).

Need to be able to predict dew point temperature as a function of pressure and H$_2$O concentration (calculate how much drying of CO$_2$ needed).

Thermodynamically, this mainly depends on the deviation of the mixture from ideal-gas behavior.
Thermodynamics: Virial Expansion

\[ \frac{p}{\rho RT} = 1 + B(T)\rho + C(T)\rho^2 + \ldots \]

\[ B(T) = \sum_i \sum_j x_i x_j B_{ij}(T) \]

- \( B_{ij} \) (second virial coefficient) rigorously related to pair potential, \( C_{ijk} \) adds 3–body effects, etc.
- Can calculate all thermodynamic properties (if density low enough); use as EOS boundary condition.
Gas/H$_2$O Second Virial Coefficient

• **Experiments** are difficult (high-T PVT data, or measure (small!) solubility of water or ice in carrier gas at low T).

• **Theory** (collaboration with Richard Wheatley, U. of Nottingham): *ab initio* quantum mechanics $\rightarrow$ quantitatively accurate potential for pairs of small molecules, then calculate $B_{12}$ rigorously (uncertainties from unc. in potential).
Water-Nitrogen $B_{12}(T)$ from theory
Water-CO$_2$ $B_{12}(T)$ from theory

Temperature (K)

$B_{12}$/ (cm$^3$ mol$^{-1}$)

Wheatley & Harvey (2011)
Coan & King (1971)
Vanderzee & Haas (1981)
Patel et al. (1987)
Bamberger et al. (2000)
Valtz et al. (2004)
Dew-Point Data

• **Problem:** Uncertainties from theory are larger than desired, reducing uncertainty with more computations not currently feasible. Also, theory loses accuracy at higher pressures.

• **Solution:** Better measurements in key temperature range, using NIST dew-point apparatus developed for humidity standards.
Dew-Point Experiments

1. Saturation system for compressed CO₂ (generates saturated gas at $P$ and $T_{DP}$)
2. Gravimetric hygrometer (designed for humidity standards) measures amounts of H₂O and CO₂ in saturated gas

NIST has only working metrology-class gravimetric hygrometer in the world [C.W. Meyer et al., Metrologia 47, 192 (2010)].

Expected uncertainty for $T_{DP}(x,P)$: 0.05 °C.
Saturation System (for $p$ to 5 MPa)

- Pressure Controller
- Heat Exchanger
- Bath
- Saturator
- Pre-Saturator
- Final Saturator
- CO$_2$ Cylinder
- SPRT
- Pressure Gauge
- Output
NIST Gravimetric Hygrometer

\[ r = \frac{m_w}{m_g} \]

- \( r \): mass of water vapor
- \( m_w \): mass of water vapor
- \( m_g \): mass of carrier gas

1) Separate moisture from dry gas (using desiccants)
2) Determine \( m_w \) by measuring increase in mass of water collection system
3) Determine \( m_g \) from volume, temperature and pressure measurements by use of pure-component EOS
Water Collection Tubes

- Desiccant used: Magnesium Perchlorate
- Mass measurements (10 μg resolution) made before and after water collection. ~70 μg uncertainty in water mass measurement.
Prover Tube Gas Collection System

- Pressure and temperature measurements determine gas density (CO₂ equation of state well known)
- Laser interferometer measures piston displacement to determine gas volume, therefore total moles of gas
- Alternating pistons allow continuous gas flow
Experimental Program

- Report saturated vapor composition (dew point) and enhancement factor (ratio of $\text{H}_2\text{O}$ partial pressure in vapor phase to pure $\text{H}_2\text{O}$ vapor pressure)
- 6 Temperatures from 10 °C to 80 °C
- Pressures up to 5 MPa (higher-pressure saturator could be built in the future)
- Avoid conditions where gas hydrates form (low $T$, high $p$)
- Use data to fit mixture EOS, also back out $B_{12}$ with good precision and rough estimates for $C_{122}$
Preliminary Results

Water Vapor Enhancement Factor in CO₂

![Graph showing water vapor enhancement factor as a function of pressure for different temperatures.]

Key:
- △ 10.0 °C
- ■ 21.7 °C
- ● 30.0 °C
- × 40.0 °C
- □ 60.0 °C
- ○ 80.0 °C
Preliminary Results for \( B_{12} \)

\[
B_{12} / (\text{cm}^3 \text{ mol}^{-1})
\]

Temperature (K)

Wheatley & Harvey (2011)
Coan & King (1971)
Vanderzee & Haas (1981)
Patel et al. (1987)
Bamberger et al. (2000)
Valtz et al. (2004)
This work
Summary of Dew-Point Results

- H$_2$O dew point in CO$_2$ measured more accurately than previous data.
- Preliminary results agree very well with theory for $B_{12}$ (Wheatley & Harvey, 2011), but have smaller uncertainty.
- Data should be useful for optimizing mixture models for design of CCS processes.
Possible Future Work

• Thermophysical properties of mixed working fluids for supercritical CO$_2$ power cycles.
• Extension of dew-point experiments to higher pressures.
• Materials compatibility for CO$_2$-rich fluids (for pipelines and power cycles).